

## LISTING BACKGROUND DOCUMENT

### WOOD PRESERVING

Wastewater from wood preserving processes that use creosote and/or pentachlorophenol (T)

Bottom sediment sludges from the treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol (T)

#### I. Summary of Basis for Listing\*

Wood preserving processes that use creosote or pentachlorophenol as preserving agents generate a wastewater, which contains toxic phenolic compounds including pentachlorophenol and tetrachlorophenol and polynuclear aromatic hydrocarbon (PAH) components of creosote. Treatment of this wastewater results in the generation of a number of bottom sediment sludges that must be removed for ultimate disposal. The Administrator has determined that wastewater from these wood preserving processes and the resulting bottom sediment sludges from wastewater treatment are solid wastes that may pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA:

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\*Based on available data, and in response to industry comment on the proposed listing (44 FR 49403, August 22, 1979), the Agency has modified this listing. Waste streams from wood preserving processes using waterborne inorganic preservatives are not included in the listings of this document. However, the Agency plans to study the sludges generated from these wood preserving processes (i.e., from work tanks, cyclinders or storage tanks), to determine whether they should also be listed. In addition, the Agency intends to study sludges generated from the periodic dredging of retorts, cyclinders, and holding tanks in which pentachlorophenol and creosote are used in the future to determine whether these sludges also should be listed.

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This conclusion is based on the following considerations:

- 1) The wastewater generated from wood preserving processes using pentachlorophenol as a preservative and the sludge generated from the treatment of this wastewater will contain significant concentrations of phenolic compounds. The wastewater from wood preserving processes that use creosote and the sludges generated from the treatment of this wastewater will contain significant concentrations of polynuclear aromatic components of creosote. Wastewater and the resulting sludges from wood preserving operations that use both creosote and pentachlorophenol as preservatives will generate waste streams which contain all or most of the above contaminants.
- 2) Polynuclear aromatics, as a group, are known to be toxic, mutagenic, teratogenic and carcinogenic. Phenolics are toxic and, in some cases, bioaccumulative and carcinogenic.
- 3) Approximately 200,000,000 gallons of wastewater are generated annually from wood preserving processes using pentachlorophenol and creosote. About 90 percent of this wastewater is treated by treatment methods which generate a bottom sediment sludge. The large quantity of waste generated increases the opportunity for exposure if waste mismanagement occurs.
- 4) Treatment of wastewater in evaporation ponds or lagoons could lead to the environmental release of hazardous constituents and result in substantial hazard via groundwater or surface water exposure pathways. Evaporation of wastewater in ponds, lagoons or by other treatment methods such as spray irrigation, if mismanaged, could also lead to the release of hazardous constituents into the atmosphere and result in substantial hazard via an air exposure pathway.
- 5) The Agency has also been informed that incineration is another (though less frequently used) disposal method for these sludges. If improperly managed, incineration could result in the release of hazardous vapors to the atmosphere, presenting a substantial hazard via an air exposure pathway.
- 6) Off-site disposal in landfills is the most commonly used disposal method for these sludges. This presents the possibility of the toxic components in the sludge migrating to nearby underground drinking water sources if the landfill is improperly designed or operated.

- 7) Several incidents of mismanagement of wood preserving plant wastes have occurred, demonstrating empirically that these wastes are capable of causing substantial harm if mismanaged.

## II. Sources of the Wastes and Typical Disposal Practices

### A. Industry Profile and Manufacturing Process

There are more than 415 wood preserving plants operated by about 300 companies in the United States. The plants are concentrated in two areas, the Southeast from east Texas to Maryland, and along the North Pacific coast. These areas correspond to the natural ranges of the southern pine and Douglas fir-western red cedar, respectively (2).

Approximately 250 million cubic feet of wood are treated each year (1), principally for railroad ties, utility poles, and lumber for construction materials. It is estimated that approximately 85 percent is treated with creosote or pentachlorophenol based preservatives as shown in Table 1 (4). The total quantity of preservative consumed in 1975 during these treatment cycles is shown in Table 2.

### B. Process Description

At plants using creosote or pentachlorophenol-based preservatives, wood products are treated to increase their resistance to natural decay, attack by insects, micro-organisms,

TABLE 1  
ESTIMATED PRODUCTION OF TREATED WOOD, 1978 (43)

Products	Treated With			
	All Preservatives <sup>b</sup>	Creosote Solutions	Penta	CCA/ACA/FCAP*
-----1,000 cu. ft.-----				
Crossties and switchties <sup>c</sup>	106,085	103,138	449	2,498
Poles	64,179	18,237	41,905	4,038
Crossarms	1,685	41.0	1,615	29.1
Piling	12,090	9,993	1,154	943
Lumber and timbers	105,305	10,779	21,209	73,317
Fence posts	20,028	4,584	10,983	4,461
Other products <sup>d</sup>	18,113	7,815	2,681	7,616
All products	327,485	154,587	79,996	92,903

\*CCA: chromated copper arsenate, ACA: ammoniacal copper arsenate, FCAP: fluor-chrome-arsenate phenol

<sup>a</sup> Volume reported for 1977 (AWAP), plus volume reported by respondents to Assessment Team Survey, plus volume estimated for nonrespondents.

<sup>b</sup> Creosote, Penta, and CCA/ACA/FCAP only.

<sup>c</sup> Includes landscape ties.

<sup>d</sup> Includes plywood.

Note: Components may not add to totals due to rounding.

TABLE 2

QUANTITY OF PRESERVATIVES USED IN 1978. (44)

Preservative	Quantity(million lbs/year)
Creosote & petrolatum	178.2
Creosote and coal tar	910
Pentachlorophenol (solid, solution)	40.8
Inorganic Arsenic salts	37.2

or fire. Briefly, the treatment consists of debarking, forming, drying, impregnation of preservative, and storage (3).

The two major wood preserving processes, producing large quantities of wastewater and sediment sludge, are called steaming and boultonizing.\* Both of these processes are pressure processes and differ mainly in the way the wood is conditioned before or during the application of the preservative. Figures 1a-1e present flow diagrams for the major wood preserving processes (Source: Reference 19).

Steaming is used principally on southern pines. In this process, the stock is normally steamed for 1 to 16 hours at about 120°C to reduce the wood's moisture content and render it more penetrable to preservatives. After steaming, the preservative is added to the same retort. Condensate removed from the retort after steaming is contaminated with entrained oils, organic compounds, and wood carbohydrates.

In the Boulton process, used principally on Western Douglas fir, the wood is immersed in the preservative, placed under vacuum, and then heated in the retort at approximately 100°C. The vapor removed is composed of water, oils, organic compounds and carbohydrates from the wood. Contaminated vapors from both the steaming and boultonizing processes are

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\*Vapor drying is another wood preserving process, also generating a wastewater and sludge of concern.

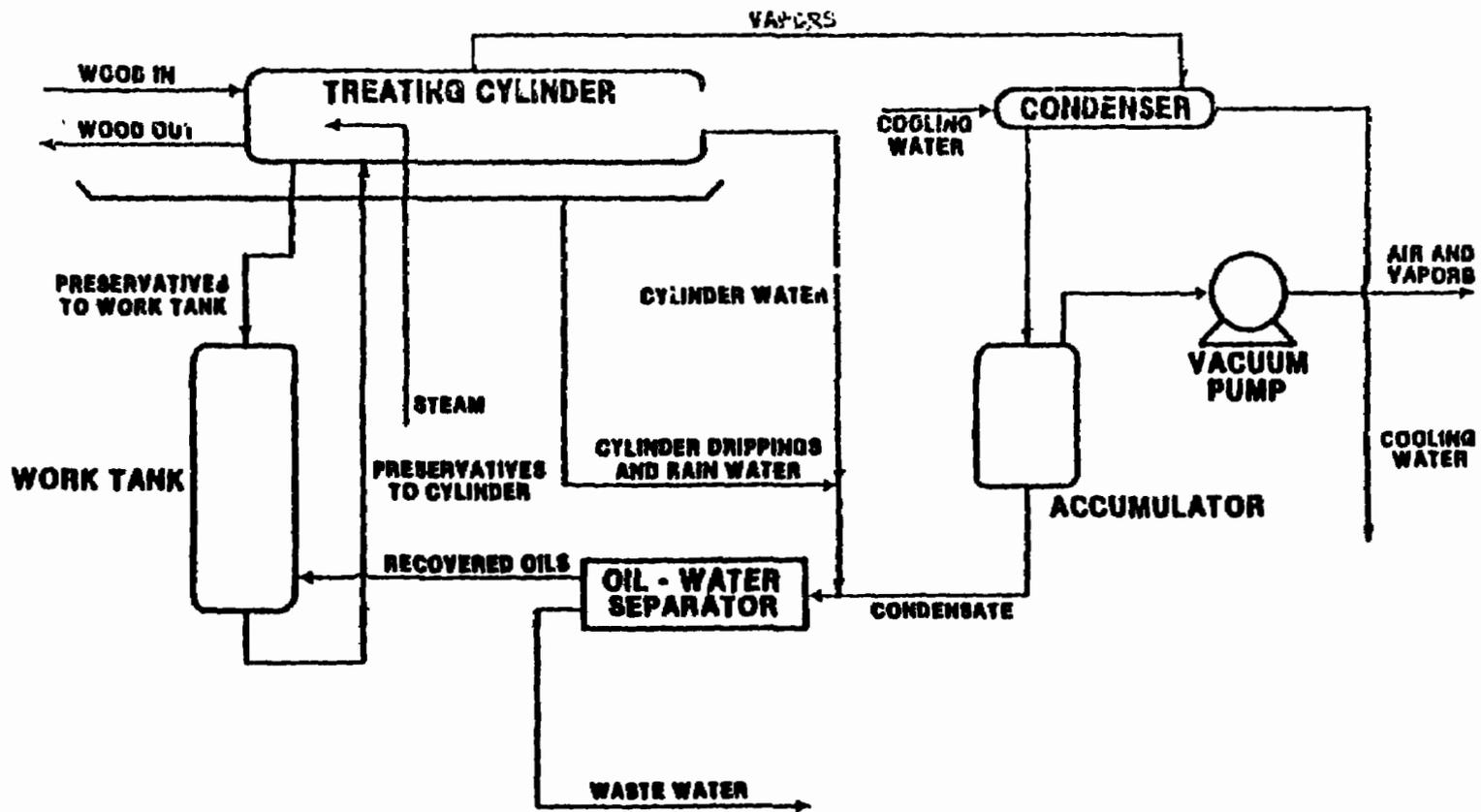


Figure 1a . OPEN STEAMING PROCESS WOOD TREATING PLANT

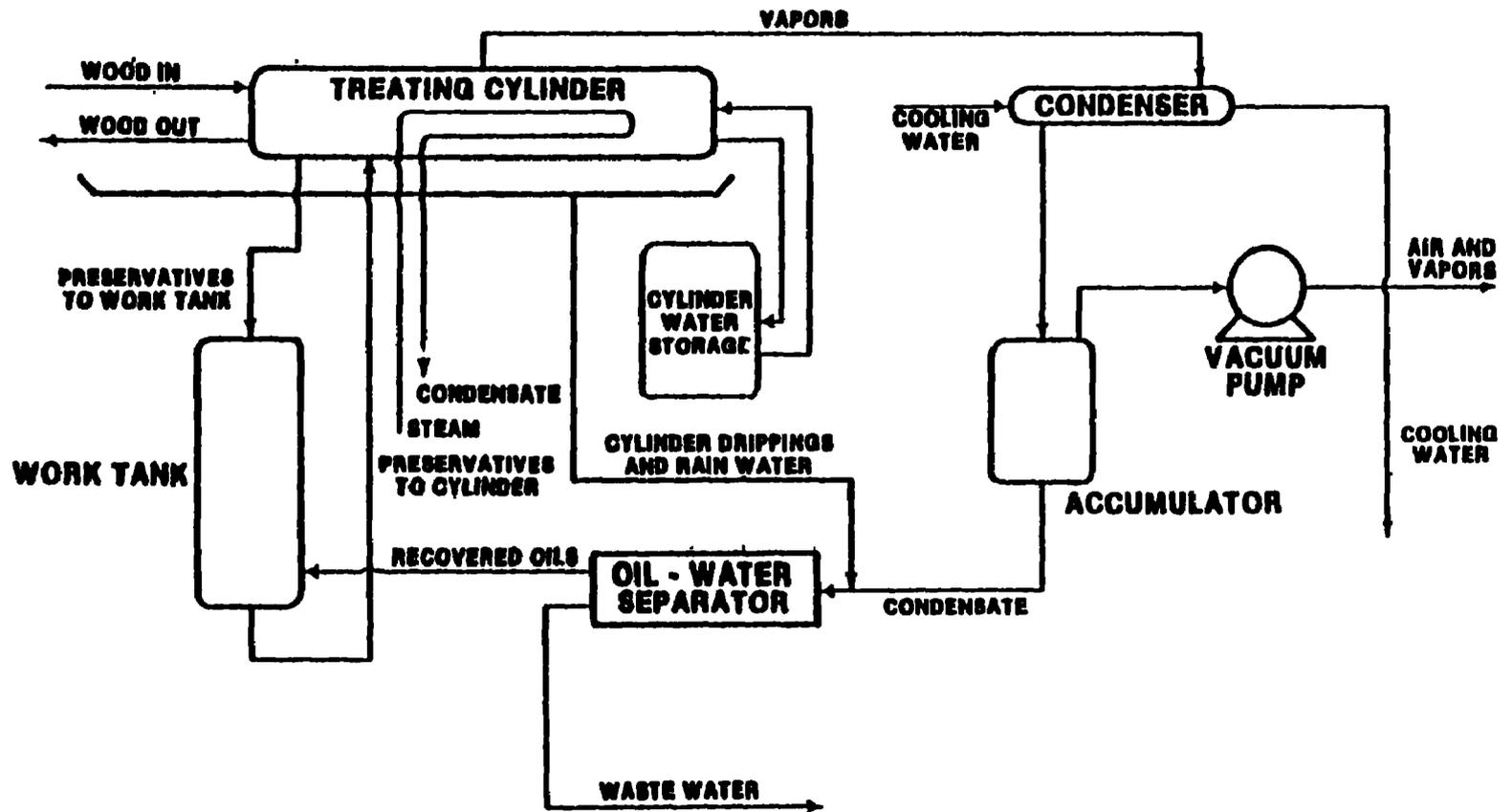


Figure 1b. **CLOSED STEAMING PROCESS WOOD TREATING PLANT**

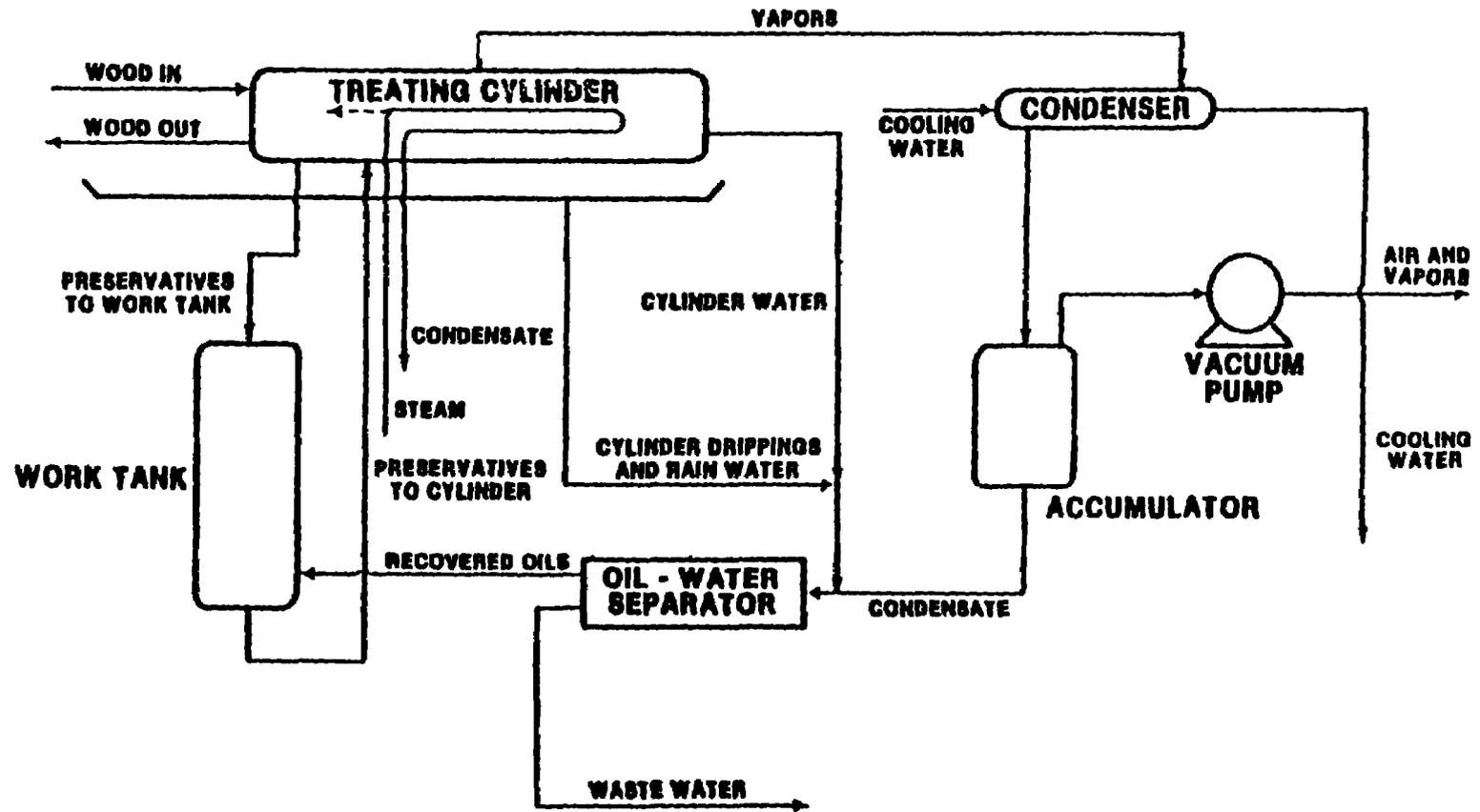


Figure 1c

**MODIFIED STEAMING PROCESS WOOD TREATING PLANT**

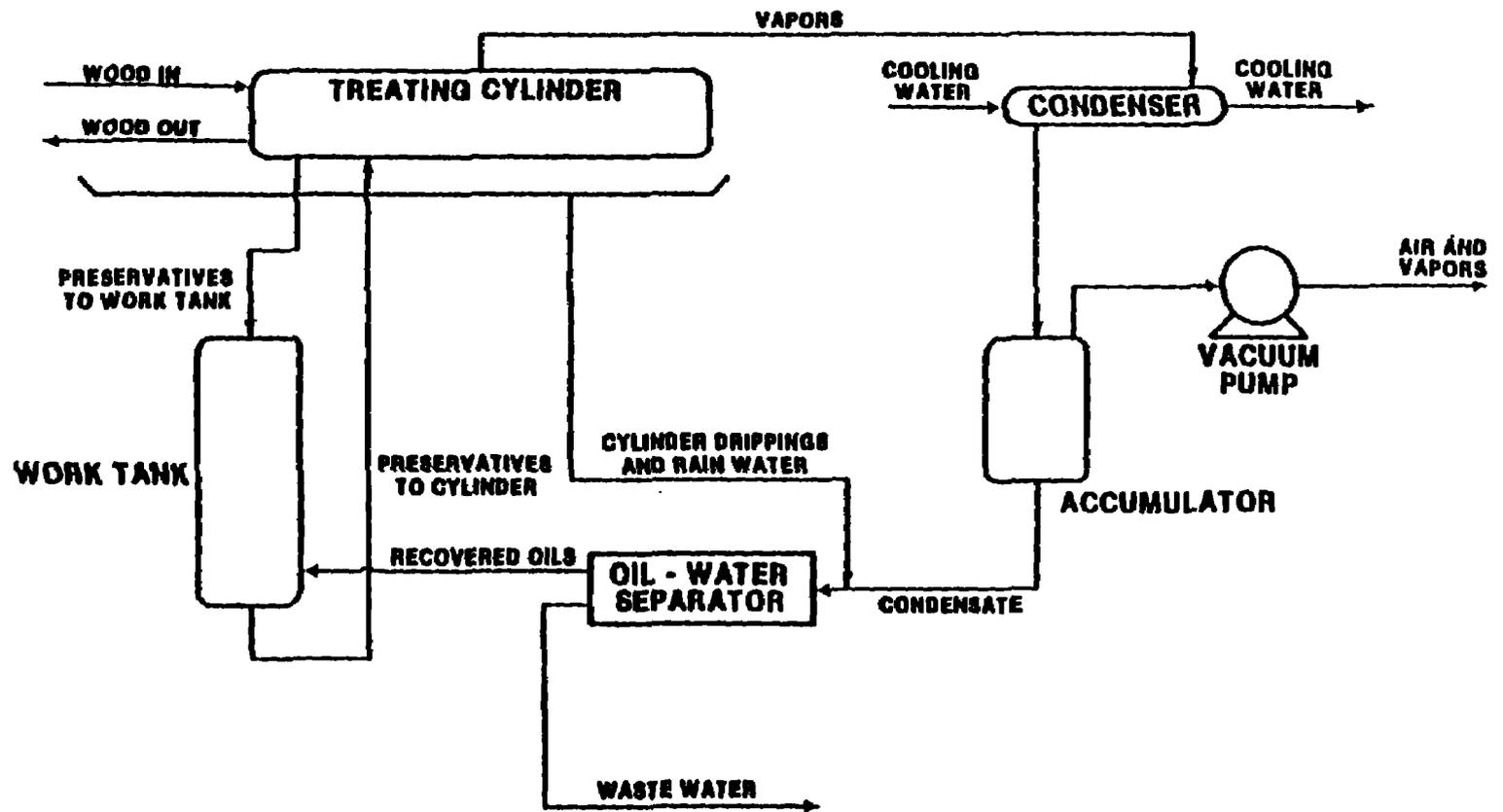


Figure 1d **BOULTON WOOD TREATING PLANT**

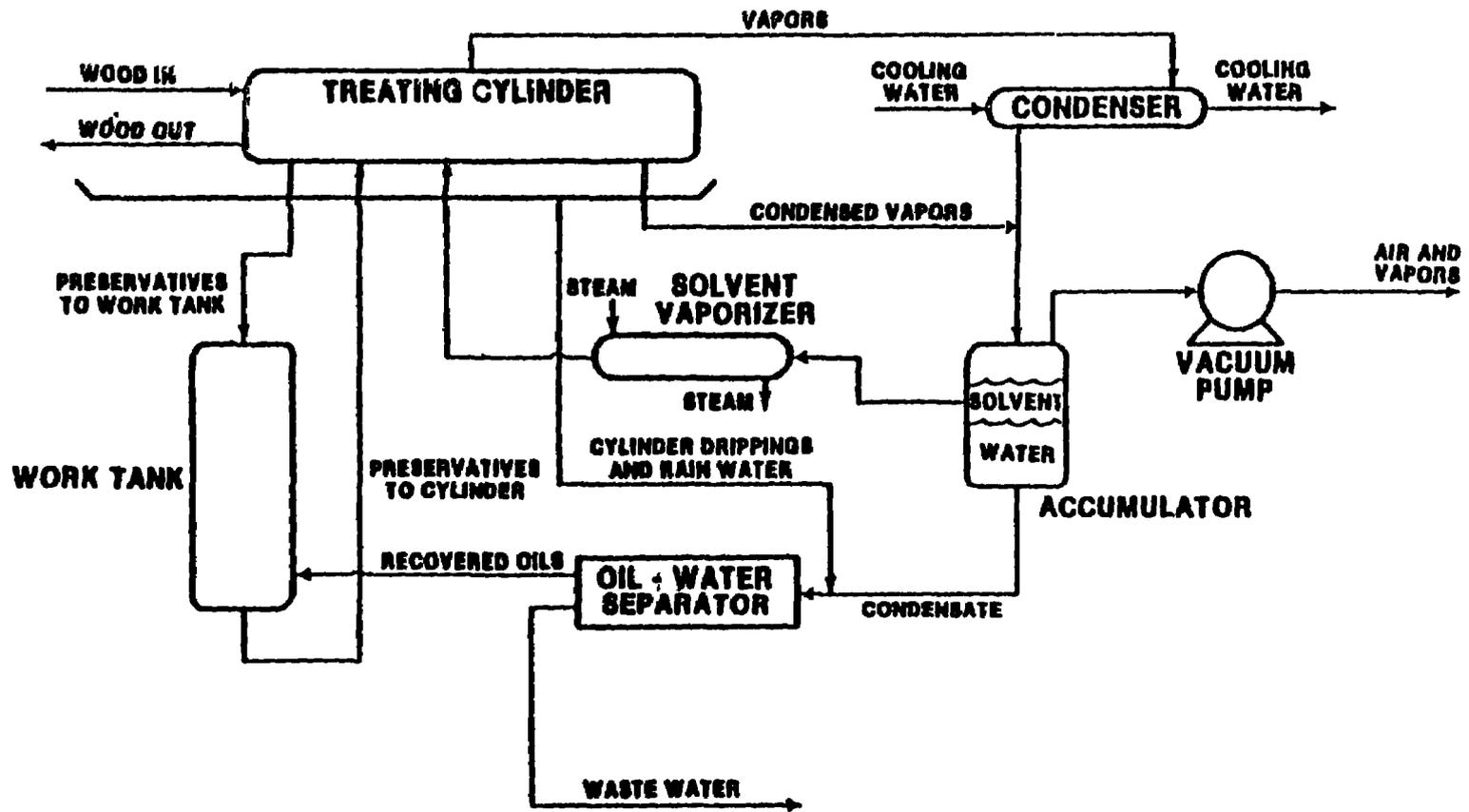


Figure 1e

**VAPOR CONDITIONING PROCESS WOOD TREATING PLANT**

condensed and transported to an oil/water separator to reclaim any free oils and preserving chemicals before treatment and/or disposal of the wastewater.(17,18)

C. Generation, Composition, and Management of Listed Waste Streams (17,18)

1. Industry Generation of Waste

Based on the quantity of wood treated with creosote or pentachlorophenol preservatives in 1975, and assuming that about one gallon of wastewater is generated per cubic foot of wood treated, over 200 million gallons of wastewater will be generated annually.

Almost all of this wastewater is treated by treatment methods that generate a bottom sediment sludge. Over 300,000 gallons per day of wastewater is discharged to POTW's. The listing covers both of these instances.\*

Table 3 shows estimates of the amounts of wastewater treatment sludges generated by creosote and pentachlorophenol preserving processes, and the amount of certain of the hazardous constituents contained in the wastes.

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\*The listing does not include wastewater discharged from a point source regulated under §402 of CWA. This listing also does not include any wastewater which is mixed with domestic sewage and that passes through a sewer system before it reaches a publicly owned treatment works (POTW). "Domestic Sewage" means untreated sanitary wastes that pass through a sewer system, (See §261.4(a)(1)(1) and (11)).

TABLE 3. POTENTIALLY HAZARDOUS SOLID WASTES FROM THE  
WOOD PRESERVING INDUSTRY (8)\*

(Source: American Wood Preserver's Association (1979))

Total Process Solid Waste metric tons/yr	Total Potentially Hazardous Constituents metric tons/yr
Creosote-oil emulsion 230-930	Creosote 1.1-4.6
Penta-oil emulsion 600*	Pentachlorophenol 3.0

Note: Although these wastes are listed in the table in terms of amounts generated per year, many of the wastes are generated on a periodic basis which often can be as long as five years (8). Thus, the sludges may be allowed to sit at the bottom of wastewater treatment ponds for five years at a time. Sometimes the bottom sediment sludges from the biological treatment of wood preserving wastewater are never removed.

\*Estimated maximum amount.

## 2. Composition

The organic components of the wastewater and bottom sediment sludges from the wood preserving industry results from the different constituents in the different formulations of pentachlorophenol and creosote and decomposition products of the constituents of the preservatives.

Table 4 gives typical compositions of commercial grade pentachlorophenol.(35) The amount of chlorinated dibenzop-dioxins and furans varies with each industrial batch, even when produced by the same manufacturer. In addition to the constituents present in commercial pentachlorophenol, other phenolic compounds have been found in wood preserving sludges and wastewater, such as unsubstituted phenol (Table 6); 2,4-dimethylphenol; p-chloro-m-cresol; 2-chlorophenol; 2,4-dichlorophenol; and 2,4-dinitrophenol (Table 7). These additional phenolic compounds may be the result of decomposition of the commercial pentachlorophenol.

The constituents of creosote are highly variable, depending on the source of the coal, the design and attendant operating conditions of the coke ovens and still, and the blending of various tar distillate fractions.(37) Several hundred constituents have been identified, with between 11-22 percent in concentrations greater than 1%.(36) (Table 5). Benzo[a]pyrene is present at 200 ppm.(38) (The presence of benzo[a]pyrene as a constituent in creosote is further

TABLE 4

COMPOSITION OF SOME COMMERCIAL PENTACHLOROPHENOL SAMPLES. (35)

	Dowicide EC-7	Dowicide 7	Monsanto
Pentachlorophenol	90.4 $\pm$ 1.0%	85-90%	84.6%
Tetrachlorophenol	10.4 $\pm$ 0.2%	4-8%	3%
Trichlorophenol	< 0.1%	< 0.1%	
Higher Chlorophenols		2-6%	
Caustic Insolubles (max)		1	
2,3,7,8-Tetrachlorodibenzo-p-dioxins	< 0.05 ppm	----	< 0.1 ppm
Pentachlorodibenzo-p-dioxins			< 0.1
Hexachlorodibenzo-p-dioxins	1.0 $\pm$ 0.1 ppm	9.27 ppm	8 (5 p
Heptachlorodibenzo-p-dioxins	6.5 $\pm$ 1.0 ppm	----	520 ppm
Octachlorodibenzo-p-dioxins	15.0 $\pm$ 3.0 ppm	575-2510 ppm	1380 ppm
Tetrachlorodibenzofurans			< 4 ppm
Pentachlorodibenzofurans			40 ppm
Hexachlorodibenzofurans	3.4 $\pm$ 0.4 ppm	Detected	90 ppm
Heptachlorodibenzofurans	1.8 $\pm$ 0.3 ppm	Detected	400 ppm
Octachlorodibenzofuran	< 1 ppm	Detected	260 ppm

TABLE 5

CONSTITUENTS OF CREOSOTE

MAJOR COMPONENTS REPORTED PRESENT IN WHOLE CREOSOTE (REF.36)

Naphthalene  
2-Methylnaphthalene  
1-Methylnaphthalene  
Biphenyl  
Dimethylnaphthalenes  
Acenaphthene  
Dibenzofuran  
Fluorene  
9,10-Dihydroanthracene  
Methylfluorene  
Phenanthrene  
Anthracene  
Acridine  
Carbazol  
Methylphenanthrenes  
2-Phenylnaphthalene  
Methylantracenes  
Pyrene  
Benzofluorenes  
Chrysene  
9,10-Benzophenanthrene

HAZARDOUS COMPONENTS PRESENT IN SMALL QUANTITIES (less than 1%)

IN CREOSOTE (Ref. 40, 41, 42)

Benzo[a]pyrene  
Benz[a]anthracene  
Benzo[b]fluoranthene  
Dibenz[a,h]anthracene  
Indeno[1,2,3-cd]pyrene

confirmed by the detection of elevated levels of benzo[a]pyrene in mussels growing near creosote treated timber pilings (about 50 ug/kg; 20 times background).(39,40) Other hazardous components of creosote in concentrations less than 1% are included in Table 5 based on their detection in edible meat of lobsters maintained in commercial tidal compounds constructed of creosote treated timber(40,41), their detection in other coal tar fractions,(42) and in part their presence in some wood preserving sludges where creosote is used (Table 8). The constituents normally occurring in coal tar are expected to be in the wastes of this industry, since creosote-coal tar solutions are used more frequently than creosote-petroleum solutions-(Table 2).

Table 6 lists of some of the typical organic compounds found in wood treating plant wastewaters.\* The absence in this Table of certain components of the original wood preservative chemicals, particularly some of the different phenolic compounds, probably indicates that an analysis for their presence was not performed rather than an actual absence of the component.

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\*Approximately 125 wood preserving plants use both organic and inorganic preservatives. Although the systems are kept separate, cross contamination of chemicals may occur through exchange of dollies used to transport the wood and drippage from the inorganic into the organic operation. Thus, wastewater from organic wood treatment processes often contains inorganic materials.

TABLE 6. ORGANIC COMPOUNDS FOUND IN WOOD PRESERVING PLANT WASTEWATER.(18)\*

Analysis of toxic phenolic compounds from 20 steam processing plants.

	Concentration (mg/l)		
	Average	High	Low
phenol	158.0	501.3	1.0
pentachlorophenol	55.0	306.0	1.2
total oil and grease	793.8	1,902.	11.0

Analysis of toxic phenolic compounds from 5 Boulton conditioning plants.

phenol	491.4	1272.0	0.9
pentachlorophenol	10.9	27.0	0.01
total oil and grease	321.5	1357.	12.3

Analysis of toxic polynuclear aromatic hydrocarbons from 9 steam conditioning plants.

fluoranthene	4.1	35.0	0.63
benzo[b]fluoranthene	0.69	1.68	0.03
benzo[a]pyrene	1.12	2.70	0.007
indeno [1,2,3-cd]pyrene	2.0	5.50	0.006
benz[a]anthracene	1.53	7.70	0.07
dibenz[a,h]anthracene	0.43	0.43	--
naphthalene	10.5	45.0	0.38
acenaphtylene	0.79	1.21	0.006
chrysene	0.48	4.70	0.07
total PAH's	39.89	232.86	7.90

Analysis of toxic polynuclear aromatic hydrocarbons from one Boulton conditioning plant using creosote

fluoranthene	0.282
benzo[b]fluoranthene	--
benzo[a]pyrene	--
indeno[1,2,3-cd]pyrene	--
benz[a]anthracene	0.034
dibenz[a,h]anthracene	--
naphthalene	3.14
acenaphthylene	2.06
chrysene	0.018
total PAH's	8.167

\*Other relevant data for comparing these concentrations such as total daily wastewater flow and daily production volume may be found in the cited reference.

Table 7 lists toxic organic compounds which have been found in the various wood preserving wastewater treatment sludges, such as the bottom of primary oil/water separator treatment sludges, flocculation sediment sludges, and biological treatment sludges.(17,26) These contain the constituents of the wood preservatives and decomposition products. The analyses of the wood treating plant sludges did not reveal every constituent listed in Table 6 in every sludge. However, pentachlorophenol and polynuclear aromatic hydrocarbons were common to all sludges tested.

Many wood processing plants, such as the two listed below, may use both creosote and pentachlorophenol based processes and thus treat the wastewater generated by these processes in a combined treatment system. Thus, sludge samples from one plant may contain both creosote compounds and phenolic compounds.(6)

According to data taken from California State hazardous waste manifests(7), one bottom sediment sludge from a wood preserving plant was found to contain 5-20% pentachlorophenol.

### 3. Disposal and Waste Treatment Practices

These plants typically send their wastewater to a series of treatment processes, which often generate bottom sediment sludges. The wastewater then is either completely retained and disposed of on the facility site (i.e., by evaporation, spray irrigation, etc.) or discharged to publicly owned treatment works, or navigable waterways. The wastewater

TABLE 7. TOXIC ORGANIC COMPOUNDS FOUND IN VARIOUS WOOD PRESERVING PLANT WASTEWATER TREATMENT SLUDGES (17,26)

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Polynuclear Aromatic Hydrocarbons:

Fluoranthene  
Benzo(b)fluoranthene  
Benzo(a)pyrene  
Indeno(1,2,3-cd)pyrene  
Benzo(a)anthracene  
Dibenzo(a,h)anthracene  
Acenaphthene  
Naphthalene  
Chrysene

Phenolics

Phenol	2,4-Dichlorophenol
2-Chlorophenol	2,4-Dinitrophenol
Pentachlorophenol	p-Chloro-m-cresol
2,4-dimethylphenol	2,4,6-Trichlorophenc

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is first generated at primary oil/water separation. The wastewater treatment sludges are generated first at oil/water primary separation and in subsequent treatment steps.

The initial wastewater treatment at most facilities is a primary oil-water separation, where much of the wood treatment chemicals are recovered and recycled to the preservative work tank. Variations include the addition of secondary oil water separators, accumulation or surge tanks prior to the oil water separators, or dehydrators for the oil recovered from the separators. These wastewater treatment processes each generate sludges which are periodically removed, containing the components of creosote and/or pentachlorophenol. An analysis of the sludge from the bottom of a pentachlorophenol oil-water separation pit showed concentrations of 1.84 ppm pentachlorophenol; 1,650 ppm 2,4-dichlorophenol; 5,090 ppm fluoranthene; 43,640 ppm naphthalene; 604 ppm pyrene; 8,410 ppm anthracene/phenanthrene; and 1,690 ppm p-chloro-m-cresol.\*(26)

Flocculation or adsorption of the wood preserving oils by the addition of clays, resins, alum, lime, or polymers is sometimes used as a secondary wastewater treatment process after primary oil-water separation. This process also generates bottom sediment sludges with a high oil and pentachlorophenol content. An analysis of the sludge from treating pentachloro-

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\*These analytical values should be used only to indicate ranges of concentrations. The Agency has not yet established standard protocols for these analyses

phenol wastewater with polymeric flocculants and clay after two oil separation steps showed concentrations of 8.2 ppm 2,4-dimethylphenol; 1,400 ppm fluoranthene; 3,000 ppm acenaphthene; 1,200 ppm naphthalene; 52 ppm pyrene; 45 ppm chrysene; 84 ppm benzo[ghi]perylene; 1,400 ppm fluorene; 52 ppm dibenz[ah]anthracene; and 3,200 ppm phenanthrene.\*(26).

Biological treatment of pre-processed wastewaters is used at some facilities. Alternatively, the pretreated wastewaters are sometimes discharged to publicly owned treatment works (POTWs) which use some form of biological treatment process.

Two plants using biological aerated lagoons as one step in their wastewater treatment process were found to have compounds from both creosote and pentachlorophenol as constituents of their sludges (Table 8). The wastewater treatment system for the first plant (Plant 10) generally consists of: (1) chemical flocculation with Bentonite clay and decantation, leaving a clay sludge, (2) nutrient addition and aeration of the clarified wastewater, generating a biological sludge, (3) spray pond evaporation, and (4) total retention of the wastewater by evaporation from the retention pond. The wastewater treatment system for the second plant (Plant 11) consists of: (1) settling in a basin where collected oil is recycled, (2) storage for 40 days in a pond and recycling of the water to the plant, (3) lagoon aeration with 60 days detention time, (4) spray irrigation, and (5) runoff storage.

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\*These analytical values should be used only to indicate ranges of concentrations. The Agency has not yet established standards protocols for these analyses.

TABLE 8. ORGANIC COMPOUNDS FOUND IN SLUDGES FROM AERATED LAGOON SECTIONS OF WASTEWATER TREATMENT FACILITIES (Ref. 6)

<u>Plant 10</u>	<u>Bottom Sediment Dry Weight (ug/kg)(6)</u>	
	<u>Aerated Lagoon</u>	<u>Final Pond</u>
<u>Polynuclear Aromatic Hydrocarbons</u>		
Benz[a]anthracene*	3,700	149
Chrysene*	4,500	2,060
<u>Phenolics</u>		
Phenol	9,030	16,000
2,4-dimethylphenol	4,398	3,418
2-chlorophenol	396,000	1,200
2,4,6-trichlorophenol	No data	25,000
Pentachlorophenol	302,000	58,000

Plant 11

	<u>Bottom Sediment Dry Weight (ug/kg)(6)</u>
<u>Polynuclear Aromatics</u>	<u>Aerated Lagoon</u>
Benz[a]anthracene*	1,250
Benzo[a]pyrene*	5,980
Chrysene*	9,280
<u>Phenolics</u>	
Phenol	4,500
2-chlorophenol	300
Pentachlorophenol	4,800

\*These were the only polynuclear aromatic hydrocarbons tested for. These components are known to be present in creosote in relatively small concentrations, so that a much higher total polynuclear aromatic hydrocarbon concentration could be inferred. In any case, these concentrations of these constituents are significant in light of their carcinogenicity. See Table 10, showing carcinogenic risk from exposure to these components at concentrations orders of magnitude lower than those observed at Plant 11.

After biological treatment, treatment by irrigation may be used. This process typically consists of (1) settling, (2) storage, (3) aerated treatment, (4) spray irrigation, and (5) runoff storage as described for Plant 11 above. The wastewater flow at this particular plant equipped with this type of treatment system averaged approximately 50,000 gallons a day.(6)

It has been argued that many of the hazardous constituents in wastewater are biodegradable and therefore would not be found in wastewater treatment sludges resulting from biological treatment. This argument first of all does not apply when sludges are generated by non-biological treatment. Information available to the Agency indicates that a large percentage of wood treating plants practice either flocculation and/or sand filtration as well as primary oil/water separation treatment steps prior to biological treatment.(19) In any case, the Agency continues to believe that most biological treatment sludges still will contain significant concentrations of toxic phenols and in some instances significant concentrations of the constituents of creosote, since the mechanism of reduction of pentachlorophenol and high molecular weight toxic pollutants is thought to be that of adsorption upon the biomass rather than complete biological degradation.(19)\*

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\*Some comments were received stating that a hazardous waste designation would discourage biological treatment of wastewater. Where biological treatment, in fact, proves successful in adequately degrading hazardous constituents, the delisting mechanism provides generators a means of avoiding hazardous waste status for their treatment sludges.

Studies on biodegradability indicate that under specific idealized conditions, pentachlorophenol is biodegradable (9,10,11). Pentachlorophenol has been shown to be degradable when composted in permeable soil at pentachlorophenol concentrations of 200 ppm or less. Under these conditions, at least 98% of the PCP can be destroyed in about 200 days (12). However, biodegradation is feasible only if the microorganisms have been acclimated to pentachlorophenol and the pentachlorophenol concentration is carefully controlled (13). Another study found that PCP persisted in warm moist soils for a period of 12 months (22). The sludge, therefore, would need to be combined with non-contaminated permeable soil in a ratio of 1:20 in order to ensure that the reported level of degradation at the disposal site is possible.

The viability for activated sludge to be used as a treatment for wastewater from the wood preserving industry containing pentachlorophenol indeed was questioned by one study.(33) Initially, the acclimated biomass would remove large quantities of pentachlorophenol, resulting in effluent concentrations of less than 1.0 mg/liter. However, in all cases, a point was reached where additional pentachlorophenol was not removed. Decreasing the pentachlorophenol concentrations in the influent to the bioreactor feed tended only to postpone when the sludge became saturated. Therefore, biodegradation of pentachlorophenol under the conditions of this system did not appear to be occurring.

Furthermore, Table 8 gives sludge sample data taken at two plants which treated wastewater with biological processes and shows that phenols and polynuclear aromatic hydrocarbons are not completely biodegraded.

Additionally, a contractor/hauler that disposes of an unspecified bottom sediment sludge for a wood treatment plant has provided an analysis of the waste for EPA (3).

The analysis is as follows:

<u>Component</u>	<u>Concentration, mg/l(6)</u>
Total phenols	5,043
Pentachlorophenol	34
Dinitrophenol	24
Creosote	10,000

Evaporation with or without the addition of heat is another process used to treat wastewaters and which generates bottom sediment sludges. Incineration of wastewaters is another less frequently practiced treatment process for the wastewaters. Discharge to the air of decomposition products of pentachlorophenol, such as chlorinated dioxins and dibenzofurans, (23,24,25) as well as the volatilized organic constituents pentachlorophenol and creosote, is possible under uncontrolled situations.

### III. Discussion of Basis for Listing

#### A. Hazardous Properties of the Waste

As discussed earlier, the most commonly used wood preservatives are creosote and pentachlorophenol. The principal toxic pollutants in wastewater from plants that use these preservatives are phenolic compounds, and polynuclear aromatic

hydrocarbon components of creosote. Table 10 summarizes the concentrations of these substances in ambient water which have been found toxic to aquatic life or necessary to protect human health by the Agency's Office of Water Regulation and Standards.(34) Comparison of these ambient water criteria with the concentrations of the pollutants found in the wood preserving industry's wastewater and wastewater treatment sludges (Tables 6-9) clearly indicates the potential for environmental damage or harm to human health if these wastes are mismanaged, since the observed concentrations are many orders of magnitude above ambient water quality criteria levels for protection of potential adverse effects on human health.

The World Health Organization 1970 Standards for Drinking Water recommends a concentration of PAHs not to exceed 0.2 ug/l. This value is greater than the ambient water quality criteria given in Table 10, but is substantially less than the concentrations found in plant effluents (Table 6).

EPA's Office of Water and Waste Management, Effluent Guidelines Division has set a maximum limit of 100 mg/l oil and grease for point source effluents from the wood preserving industry, based on considerations of technology and economic feasibility. (See 40 CFR §§429.74 and 429.84.) This 100 mg/l oil and grease level has been found to correspond to an approximate 1.0 mg/l polynuclear aromatic hydrocarbon effluent concentration and an approximate 15 mg/l pentachlorophenol

TABLE 10

AMBIENT WATER QUALITY CRITERIA & OBSERVED TOXICITY LEVELS FOR  
CONTAMINANTS PRESENT OR LIKELY TO BE PRESENT IN THESE WASTES\*\*  
(Ref. 34)

mg/l = milligrams per liter = ppm = parts per million  
ug/l = micrograms per liter = ppb = parts per billion  
ng/l = nanograms per liter = ppt = parts per trillion

	<u>Freshwater Aquatic Life</u>	<u>Saltwater Aquatic Life</u>	<u>Human Health</u>
<u>POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs)</u>			
PAHs (total)	--	300 ug/l (acute)	2.8 ng/l* (cancer risk of 10 <sup>-6</sup> )
Acenaphthene	520 ug/l (acute)	500 ug/l (acute)	.02 mg/l (taste and odor only)
Fluoranthene	3980 ug/l (acute)	16 ug/l (acute)	42 ug/l
Isophorone	117,000 ug/l (acute)	12,900 ug/l (acute)	5.2 mg/l
Naphthalene	620 ug/l	2,350 ug/l (acute)	insufficient data
Benzo[a]pyrene	--	--	2.8 ng/l* (cancer risk of 10 <sup>-6</sup> )
Dibenz[a,h]anthracene	--	--	1.3 ng/l*

\*Indicates recommended criteria level to protect human health or aquatic organisms. The cancer risk hazards given in this table are for protection at the one 10<sup>6</sup> level. The Ambient Water Quality Criteria give ranges for protection from cancer risks from 0 corresponding to zero exposure level up to 10<sup>5</sup>.

\*\*Lowest toxicity values are cited. No entry indicates insufficient data to establish a level for either acute or chronic toxicity. See original documents for more information.

	<u>Freshwater Aquatic Life</u>	<u>Saltwater Aquatic Life</u>	(cancer risk of 10 <sup>-6</sup> ) <u>Human Health</u>
<u>PHENOLIC COMPOUNDS</u>			
Phenol	2,560 ug/l (acute & chronic)	5,800 ug/l (acute)	3.5 mg/l* (toxicity)  0.3 mg/l * (taste & odor)
2-Chlorophenol	4,380 ug/l (acute)  2,000 ug/l (flavor, fish)	--	0.1 ug/l* (taste & odor)
3-Chlorophenol			0.1 ug/l* (taste and odor)
4-Chlorophenol	--	29,700 ug/l (acute)	0.1 ug/l* (taste & odor)
2,3-Dichlorophenol	--	--	0.4 ug/l* (taste & odor)
2,4-Dichlorophenol	365 ug/l (chronic)  0.4 ug/l (flavor, fish)	--	3.09 mg/l* (toxicity)  0.3 ug/l* (taste & odor)
2,5-Dichlorophenol	--	--	0.5 ug/l* (taste & odor)
2,6-Dichlorophenol	--	--	0.2 ug/l* (taste & odor)
3,4-Dichlorophenol			0.3 ug/l* (taste & odor)
2,4,5-Trichlorophenol	--	--	2,600 ug/l* (toxicity)  1.0 ug/l* (taste & odor)
2,4,6-Trichlorophenol	970 ug/l	--	1.2 ug/l* (cancer risk of 10 <sup>-6</sup> )

	<u>Freshwater Aquatic Life</u>	<u>Saltwater Aquatic Life</u>	<u>Human Health</u>
2,3,4,6- Tetrachlorophenol	--	--	1.0 ug/l* (taste & odor)
2,3,5,6- Tetrachlorophenol	--	400 ug/l (acute)	1.0 mg/l (toxicity)
			30 ug/l* (taste & odor)
2-Methyl-4-chlorophenol	--	--	1800 ug/l* (taste & odor)
3-Methyl-4-chlorophenol	30 ug/l (acute)	--	3000 ug/l* (taste & odor)
3-Methyl-6-chlorophenol	--	--	20 ug/l* (taste & odor)
Nitrophenols (general)	150 ug/l (acute)	4,850 ug/l (acute)	--
Dinitro-o-cresol	--	--	13.4 ug/l* (toxicity)
Dinitrophenol	--	--	70 ug/l* (toxicity)

concentration. Actual risk assessment calculations for protecting the health of specific population groups were not used to calculate this standard. Even so, Table 5 shows that wastewater from this industry after primary treatment by oil/water separation contains higher concentrations of oil and grease than allowed by this standard and also higher concentrations of polynuclear aromatic hydrocarbons and phenolics than if the 100 mg/l oil and grease criteria were met. Further, the concentrations of polynuclear aromatic hydrocarbons and phenolics that correspond to 100 mg/l oil and grease are much higher than the ambient water quality criteria given in Table 10.

Phenolics are toxic and in some cases bioaccumulative and carcinogenic. Phenol, pentachlorophenol, 2,3,4,6-tetrachlorophenol, 2,4,6-trichlorophenol, and 2,4-dichlorophenol are given highly toxic ratings in N. Irving Sax's Dangerous Properties of Industrial Materials. 2,4,6-Trichlorophenol has been identified by the Agency as a compound exhibiting substantial evidence of being carcinogenic. In addition, 2,4,6-trichlorophenol has been reported to be mutagenic, and pentachlorophenol has shown mutagenic and teratogenic effects.

Many polynuclear aromatic hydrocarbons are known to be toxic, mutagenic, teratogenic and carcinogenic. Benz(a)-anthracene and chrysene have been identified by the Agency as compounds exhibiting substantial evidence of being

carcinogenic. Additional information and specific references on the adverse effects of the following substances can be found in Appendix A: These substances are also designated as priority pollutants under Section 307(a) of the Clean Water Act.

Pentachlorophenol	Creosote
Phenol	Chrysene
2-Chlorophenol	Naphthalene
p-Chloro-m-cresol	Fluoranthene
2,4-Dimethylphenol	Benzo[b]fluoranthene
2,4-Dinitrophenol	Benzo[a]pyrene
Trichlorophenols	Indeno[1,2,3-cd]pyrene
Tetrachlorophenols	Benz[a]anthracene
2,4-Dinitrophenol	Dibenz[a]anthracene
	Acenaphthalene

#### B. Migratory Potential of Hazardous Constituents

In light of the extreme danger posed by these waste constituents, the Agency would require some assurance that these waste constituents will not migrate and persist to warrant a decision not to list these waste streams. No such assurance appears readily available.

Many of these waste constituents, in fact, have proven capable of migration, mobility and persistence. Chrysene, naphthalene, benz(a)anthracene, and other polynuclear aromatic hydrocarbons have been detected in rivers, demonstrating ability to persist.(20) The migratory potential and persistence of phenol, trichlorophenol and dichlorophenol is confirmed by the fact that these constituents have been identified in samples taken at the Love Canal site in Niagara, Falls, New York.(28) Dichlorophenol has also been found in

school and basement air at Love Canal, demonstrating ability to migrate and persist in the air (See "Love Canal, Public Health Bomb, a Special Report to the Governor and Legislature", New York State Department of Health, 1978.)

The American Wood Preservers Association examined the leaching in soil of pentachlorophenol at concentrations that would approximate conditions of treated wood in contact with the ground.(4,12) Soils containing 100 and 300 ppm pentachlorophenol resulted in a leachate containing less than 0.01 percent of the original concentration of the pentachlorophenol in the soil. However, the concentration levels in these studies were less than those which have been found in some wood preserving plant wastes. Additionally, the binding ability of soil with phenols may be much greater than that of biological treatment or other residue sludges. Thus, the predictive ability of an experiment showing a small amount of leaching for pentachlorophenol contaminated soils may not be applicable to treatment plant sludges. That pentachlorophenol will leach and migrate in actual mismanagement cases is in any event demonstrated by the damage incidents described below.

Creosote compounds have also demonstrated the ability for mobility and persistence. An actual damage incident of surface and groundwater contamination due to improper management of wood preserving chemicals, including creosote and pentachlorophenol, confirms the migratory potential, mobility

and persistence of the waste constituents in these wastes. In the 1950's, waste chemicals including creosote and other types of wood preserving chemicals were injected into wells in Delaware County, Pennsylvania. The injected wastes migrated into groundwater, infiltrated a storm drain sewer, and discharged into a small stream, causing biological damage. Although injection of the wastes into the wells ceased in the 1950's, contamination was first observed in 1961.(21) Thus, the waste constituents proved capable of migration via both ground and surface waters, and were able to persist and cause damage for long periods of time.

Two other mismanagement incidents demonstrate both the potential for migration and persistence of wood preserving plant wastes. In one incident, creosote was found to migrate from wood preserving treatment into the groundwater supply of a neighboring community (29). A very recent incident (September 14, 1980) of groundwater contamination by pentachlorophenol from a wood preserving plant occurred in Jacksonville, Florida. This sludge dump on the company property was allegedly responsible for contamination levels of pentachlorophenol in adjacent residential property groundwater at levels as high as 0.50 ppm. Drinking water was so far not found to be contaminated at an experimental detection limit of 12 ppm pentachlorophenol, but nitrophenol and 2-chlorophenol were detected though not quantified. Soil samples at one location adjacent to the facility contained up to 24 ppm pentachlorophenol.(30) These incidents demonstrate empirically that

these sludges, if mismanaged, may cause substantial harm to humans or other environmental receptors.

The mobility and persistence of polynuclear aromatic hydrocarbons also is shown by a number of damage incidents. Although these incidents do not involve the wood preserving industry, they do show that PAHs may migrate from creosote-containing wastes, and prove persistent upon release.

A company in Minnesota handled, stored, treated and disposed of coal tar, creosote oil and other products for over 50 years in an 80-acre site. While the operation supposedly included discharge of waste products into a ponding area, there were apparently numerous cases of spills, leaks, pipeline breaks, and burial of wastes over the years. As a result, chemicals associated with the company's process, among these polynuclear aromatic hydrocarbons, migrated as far as two miles. Five drinking water wells contaminated by the toxic wastes were closed in 1978 and 1979 after operations were stopped in 1971.(31)

A coke company in St. Paul used a 10'x13' unlined basin to dispose of oil, grease, various hydrocarbons and phenols. Inspection at the time of sale of this property revealed both soil and groundwater contamination with polynuclear aromatic hydrocarbons as far as 1400 feet from the pit.(31)

Another reason for thinking that the hazardous constituents in these wastes could prove sufficiently mobile to reach groundwater is the large quantities of waste generated. We believe the attenuative capacity of the environment surrounding

these facilities could be reduced or used up, since large quantities of bottom sediment sludge containing such large concentrations of harmful constituents are disposed of in landfills or sometimes allowed to accumulate at the bottom of ponds and lagoons for long periods of time.

Finally, many of the constituents of concern are highly bioaccumulative in environmental receptors. Benz(a)anthracene and pentachlorophenol are extremely bioaccumulative with octanol/water partition coefficients of 426,579 and 102,000, respectively. Tetrachlorophenol, trichlorophenol and dichlorophenol are also highly bioaccumulative with octanol/water partition coefficients of 12,589, 4,169 and 1,380, respectively (App. B).<sup>\*</sup> Thus, the possibility that waste constituents could accumulate in harmful concentrations if they reach a receptor further supports a hazardous waste listing.

In light of the above damage incidents demonstrating migration and persistence and the extreme dangers to human health and the environment posed by these constituents, a failure to list this waste as hazardous is not justified.

### C. Exposure Pathways

Mismanagement of these wastes, therefore, could lead to environmental contamination since constituents are available

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<sup>\*</sup>An octanol/water coefficient of 100 means that after an aqueous solution of the tet compound is intimately mixed with octanol and allowed to separate, there will be 100 times as much of the test compound in the octanol than in the water. Solubility of a substance in octanol models its solubility in body fat tissue and is, therefore, indicative of bioaccumulation potential.

for release and are likely to persist following release. Thus, as previously noted, the wastewaters generated by wood preserving operations are typically treated by evaporation, combined biological and irrigation process, or incineration. Bottom sediment sludge, generated by the treatment of the wastewater, is typically disposed of in an off-site landfill, after prolonged storage in holding lagoons. Incineration is another possible disposal method.

The treatment of wastewater in ponds and/or lagoons, if mismanaged, could lead to the release of hazardous constituents by leaching from the resulting sludges, particularly in light of these constituents' demonstrated propensity for migration. These waste constituents could thus contaminate groundwater if ponds or lagoons are unlined or lack adequate leachate collection systems. Siting of wastewater treatment facilities in areas with highly permeable soils could likewise facilitate leachate migration. The bottom sediment sludges, which form at the bottom of wastewater treatment ponds or lagoons, could thus release harmful constituents and contaminate groundwater. As previously noted, these sludges may be allowed to sit at the bottom of ponds for five years or longer(8,44), thus increasing the potential for release of harmful constituents and for eventual groundwater contamination.

There is also a danger of migration into and contamination of surface water if ponds and lagoons are improperly designed or managed. Thus, inadequate flood control measures could

result in washout or overflow of ponded wastes.

Disposal of bottom sediment sludge in off-site landfill, if mismanaged, could also lead to release of hazardous constituents. The waste constituents of concern may migrate from improperly designed or managed landfills and contaminate ground and surface waters.

Transportation of these sludges off-site increases the likelihood of mismanagement and of their causing harm to human health and the environment. Mismanagement of sludges during transportation thus may result in hazard to human and wildlife through direct exposure to harmful constituents. Furthermore, absent proper management safeguards, the waste might not reach the designated disposal destination at all.

The harmful constituents in the waste also present a health hazard via an air inhalation pathway. Studies on actual pentachlorophenol and creosote process wastewater samples using a laboratory scale pan evaporator indicated that a large percentage of the constituents of pentachlorophenol and creosote were entrained in the vapors after several hours of heating at temperatures up to 88°C.(18)

A letter from the manager of Kopper's Co., Inc. indicated that evaporation of pentachlorophenol effluent from a pan evaporator or cooling tower or other spray device could increase the amount of PCP discharged into the air and into the general environment. No supporting analytical data was provided (27). Thus, evaporation of wastewaters in ponds, lagoons, stripper/cooling towers, evaporation pans, and

incineration of wastewaters or sludges could lead to the release of hazardous and volatile constituents into the air.

Disposal of sludges by incineration is another type of management which could lead to substantial hazard. Improper incineration might result in serious air pollution by the release of toxic fumes occurring when incineration facilities are operated in such a way that combustion is incomplete. The formation of more toxic compounds such as polychlorinated dibenzo-p-dioxins or dibenzo-furans during the combustion of pentachlorophenol mixtures is also possible.(23,24,25) These conditions can, therefore, result in a significant opportunity for exposure of humans, wildlife and vegetation, in the vicinity of these operations, to potentially harmful substances.

## References

1. Federal Register, Vol. 44, No. 212. Wednesday, October 31, 1979.
2. Development Document for Effluent Limitation. EPA: 440/1-74-023a.
3. Federal Register No. 202. Wednesday, October 18, 1978.
4. Ernst and Ernst. Wood Preservation Statistics. 1976. American Wood Preservers Association.
5. Not used in text
6. Myers, L.H., et al. Indicators Fate Study. EPA: 660/2-78-175. August, 1979.
7. Handbook of Industrial Waste Compositions in California. 1978
8. Multimedia Pollution Assessment of the Wood Products Industries, Edward C. Jordan Co., Inc., for Industrial Pollution Control Division, EPA Contract No. 68-03-2605, November, 1979.
9. Hartford, W.H., "The Environmental Impact of Wood Preservation," American Wood Preservers Association, 1976. ~~(Not cited in document)~~ → p 25
10. Young, A.L. et al, Fate of 2,3,7,8-tetrachlorodibenzop-dioxin (TCDD) in the Environment: Summary and Decontamination Recommendations, United States Air Force Academy, Colorado, USAFA-TR-76-18, October, 1976. ~~(Not cited in document)~~ p. 25
11. Kirsch, E.J., and J.E. Etzel. Microbial Decomposition of Pentachlorophenol, Journal of Water Pollution Control Federation, Vol. 45, No. 2, February, 1973.
12. Arsenault, R.D., "Pentachlorophenol and Contained Chlorinated Dibenzodioxins in the Environment--A Study of Environmental Fate, Stability, and Significance when Used in Wood Preservation." American Wood Preservers Association, 1976.
13. Proceedings: Technology Transfer Seminar on the Timber Processing Industry--March 10,11, 1977. Toronto, Ontario. EPS: 3-WP-78-1, January, 1978.
14. Not used in text
15. Not used in text
16. Not used in text
17. Accurex Corporation, "Solid Waste from Wood Treating Processes - a Hazardous Waste Background Document", December 20, 1979.

18. Acurex Corporation, "Wood Treating Industry Multimedia Emission Inventory", Draft Report, June, 1980. EPA Contract 68-02-2611.
19. Development Document for Effluent Limitations, Guidelines and Standards for the Timber Products Processing Point Source Category. EPA 440/1-79/023b.  
*^(Proposed)*
20. Shakleford and Keith, "Frequency of organic compounds identified in water," EPA-600/4-76-062, Environmental Research Laboratory, Athens, Ga., Dec. 1976.
21. U.S. EPA, Open File, unpublished data, Hazardous Site Control Branch, WH-545, 401 M St. S.W., Washington, D.C. 20460. Contact Hugh Kauffman 202/245-3051.
22. Harvey, W.A. and A.S. Crofts, "Toxicity of PCP and its sodium salt in three yolo soils." Hilgardia 21, 487 (1952).
23. Chem. Eng. News, Sept. 24, 1979, p. 27.
24. Rappe, C. and M. Stellan, "Formation of polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) by burning or heating chlorophenates" Chemosphere, No. 3, 269 (1978).
25. Jansson, B. and G. Sundstrom, "Formation of polychlorinated dibenzo-p-dioxins during combustion of chlorophenol formulations" Sci. Total Environ. 10, 209-217 (1978).
26. Office of Water & Waste Management, Effluent Guidelines Division, U.S. EPA, Unpublished data from ESE, Inc.) Plant sampling reports. 1979-1980. NOTE: This data may be used to indicate relative amounts of constituents only.
27. Arenault, R.D., Private communication to D. Costle, Administrator, U.S. EPA (February 13, 1980).
28. N.Y. State Department of Health, 1978. "Love Canal, public health bomb, a special report to the governor and legislature" (1978).
29. Mittelman, A. (1978) "Exposure analysis for creosote, coal tar and coal tar neutral oils, Unpublished Data. Office of Pesticides & Toxic Substances, U.S. EPA.
30. Private Communication, Vincent Cassidy, Water Pollution Control, Department of Health, Welfare, and Biological Environmental Services, City of Jacksonville, Florida, October 15, 1980.

- 31a. U.S. EPA, "Damages and threats caused by hazardous material sites", EPA/430/9-80/004, p. 20. Jan. 1980.
- 31b. U.S. EPA, Suit against Reilly Tar, St. Louis Park, Minn., Filed Sept. 4, 1980 in District Court, Minneapolis, Minn.
32. Not used in text
33. Industrial and Environmental Research Laboratory, Food and Wood Products Branch. Contract No. 68-03-2605. "Evaluation of the batch treatment of industrial phenolic wastes." Unpublished data. Progress Report No. 5(12) of E. C. Jordon Co., 1979.
34. Office of Water Regulations & Standards, (1980) EPA. Ambient Water Quality Criteria, \_\_\_\_\_ FR \_\_\_\_\_ (November \_\_\_\_\_, 1980).  
\*Note: No Federal REGISTER Citation is yet available, but the the Water Quality Criteria have been signed by the Administrator at the time of preparation of this document.
35. Environmental Health Advisory Committee, Science Advisory Board, U.S. EPA. Report of the Ad Hoc Study Group on Pentachlorophenol Contaminants. Draft Report, December, 1978.
36. Nestler, F.H.M. The characterization of wood preserving creosote by physical and chemical methods of analysis. Proposed USDA Forest Service Research Paper FPL 195. Preliminary copy. 1974.
37. Kirk Othmer Encyclopedia of Chemical Technology, 3rd Ed., Vol. 6, p 302, 1973.
38. Guerin, M.R. Energy sources of polycyclic aromatic hydrocarbons. Oak Ridge National Laboratory. 1977.
39. 43 FR 48154, 1978.
40. Office of Solid Waste, U.S. EPA. Listing background documents for Creosote, Health & Environmental Effects. Appendix A May 19, 1980.
41. Dunn, B.P. & J Fee. Polycyclic aromatic hydrocarbon carcinogens in commercial seafoods. J. Fish Res. Board Can. 36, 1469, 1979.
42. Office of Toxic Substances, U.S. EPA. Investigation of selected potential environmental contaminants: Asphalt and coal for pitch Final Report. EPA-560/2-77-005, 1978.
43. U.S. Dept. of Agriculture, State's EPA Preservative Chemical Assessment Team. The biological and economic assessment of pentachlorophenol, inorganic arsenic, and creosote. Draft, May 15, 1980.
44. American Wood Preservers Institute. Comments submitted to the Office of Solid Waste, U.S. EPA, September 19, 1980.

## Response to Comments - Wood Preserving Industry

One commenter raised a number of questions with respect to the hazardousness of waste K001 (Bottom sediment sludge from the treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol) and the proposed listing (wastewater from wood preserving processes that use creosote or pentachlorophenol).

1. The commenter first states that RCRA was not intended to cover the treatment and disposal activities of such facilities (i.e., at wood preservers), but rather was designed to eliminate abuses in waste treatment and disposal such as at Love Canal. The commenter then argues that these wastes are already adequately regulated under the Clean Water Act (CWA) and that the listing of wastewaters resulting from wood preserving and the sludge generated when the wastewater is treated will result in an expensive burden to the wood preserving industry without any commensurate public benefit.

The Agency strongly disagrees with the commenter's claims. The Resource Conservation and Recovery Act was enacted by Congress to control the improper management of hazardous wastes. Although the Act has several objectives

(including the promotion of resource recovery and the proper management of non-hazardous solid waste), Congress' overriding concern in enacting RCRA was to establish a national system which would ensure the proper management of hazardous waste. Nowhere in the Act or in the legislative history does Congress make a distinction between the types of treatment, storage or disposal facilities the Act was meant to control. In fact, the Act is quite clear as to the extent of coverage; all wastes identified or listed by EPA as hazardous will be subject to the Federal "cradle-to-grave" management system for hazardous wastes. Therefore, hazardous waste treatment, storage and disposal facilities at wood preserving plants clearly may be subject to the requirements of RCRA.

The Agency also disagrees with the commenter's claim that these wastes, if managed in conformity with current effluent regulations, present no serious threat to human health and the environment. First, the comment is not even relevant to the listing of bottom sediment sludges. With regard to the proposed listing of process wastewater, it should be pointed out that under the CWA the Agency's authority is limited to the actual point source discharge into navigable waters, and not to the

industrial wastewaters upstream from the point of discharge. Environmental hazards posed by wastewaters in treatment and holding facilities--primarily groundwater contamination and the vaporization of volatile organic materials--therefore is not controlled under the CWA or other environmental statutes (See the Part 261 preamble for more detailed discussion of regulatory authority of wastewaters 45 FR at 3309 (May 19, 1980)).

Secondly, the fact that waste effluent is treated prior to point source discharge does not guarantee that human health and the environment is protected adequately during the treatment process. EPA believes that there is in fact a strong potential for hazardous volatile emissions from certain wastewater treatment processes using heat (i.e., pan evaporation or thermal ponds), which are currently used by the wood preserving industry. For example, in a laboratory pan evaporator test\*, pentachlorophenol was detected and quantitatively recovered from the vapor phase. In this test, large percentages of the original pentachlorophenol in the wastewater was recovered in the volatile emissions after 3 to 4 hours of heating at temperatures up to 88.2°C.

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\* Accurex Report, 1980.

Emissions of naphthalene, acenaphthene, fluorene and phenanthrene/anthracene --all hazardous constituents--also were found from creosote wastewater pan evaporator tests.\* Additionally, in a letter from the manager of Kopper's Co., Inc.\*\* , it was indicated that evaporation of pentachlorophenol effluent from a pan evaporator, cooling tower, or other spray device would increase the amount of pentachlorophenol discharged into the air and into the general environment.

Furthermore, incineration is also used by the wood preserving industry as a method for managing wastewater (although the Agency does not currently know to what extent). Disposal by incineration, if mismanaged, could result in the release of toxic fumes when incineration facilities are operated in such a way that combustion is incomplete (i.e., the formation of toxic compounds such as polychlorinated dibenzo-p-dioxins and dibenzofurans during

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\*The normal volatility of pentachlorophenol and of the components of creosote and pentachlorophenol would be greatly increased by the common phenomenon of co-distillation, or the additive vapor pressures of the components of the two phase oil/water system. (see WJ Moore, Physical Chemistry, or any similar undergraduate chemistry text.) Therefore, the Agency cannot accept data on the volatilization temperature of individual components of creosote and pentachlorophenol as predicting the volatilization temperature during a steam distillation process, as exists during pan evaporation.

\*\*Arenault, R.D., Feb. 13, 1980, Private communication to D. Costle, Administrator, U.S. EPA.

the combustion of pentachlorophenol mixtures, as well as volatilizing of pentachlorophenol and creosote\*). Therefore, the Agency strongly believes that mismanagement of these wastewaters could lead to a large amount of pentachlorophenol, creosote components and other volatile organics volatilizing into the atmosphere creating a substantial present or potential hazard to human health and the environment. Assertion of RCRA jurisdiction provides a logical means of dealing with this potential problem.

Finally, with respect to the commenter's concern as to the economic impact these regulations will have on the wood preserving industry, the Agency has reviewed carefully the legislative history of RCRA and finds no indication that Congress intended adverse economic impact to be considered in implementing Subtitle C of RCRA. Nor is there any explicit requirement in the Act directing EPA to consider costs in the development of its regulations, as appear in other environmental statutes. Rather,

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\*Chemical Engineering News, Sept. 24, 1979, p. 27; Jansson, B. and G. Sundstrom, 1978, "Formation of Polychlorinated Dibenzo-p-dioxins During Combustion of Chlorophenol Formulations", Science Total Environment, 10, 209-217; Rappe, C. and M. Stellan, 1978 "Formation of Polychlorinated Dibenzo-p-dioxins (PCDDs) and Dibenzofurans (PCDFs) by Burning or Heating Chlorophenates", Chemosphere, No. 3, p. 269.

the Agency is directed to protect human health and the environment. This being the case, we do not believe consideration of economic impact to be relevant in making hazardous waste listing determinations.

2. The commenter then argued that the overwhelming majority of data contained in the listing background document on wood preserving pertains only to wastewater treatment sludge, and not to wastewater itself. In fact, the commenter points out that only Table 5 on pg. 155 (May 19, 1980 listing background document) contains any indication that the hazardous constituents may be present in wood treating wastewater, and even this table fails to give any indication of the concentrations of those substances. Therefore, the commenter argues that this limited information in no way justifies the summary conclusion that wood treating wastewater will contain "significant" concentrations of either "toxic phenolic compounds and volatile organic solvents such as benzene", or "toxic polynuclear aromatic components of creosote and volatile organic solvents such as toluene." Thus, the commenter believes the Agency has failed to establish any factual predicate for listing wood preserving wastewater as hazardous.

The Agency agrees with the commenter that the listing background document on wood preserving

contained only limited data on the composition and concentrations of the toxic constituents present in the wastewater. However, the Agency also believes that sufficient information was available in the record (which the commenter has been known to review) to support the listing of this waste stream. For example, in the draft report, "Wood Treating Industry Multimedia Emission Inventory", prepared by the Acurex Corp., June 1980 (cited by the commenter), analysis of wastewaters from both the steam and boulton conditioning processes shows levels of phenolic compounds and polynuclear aromatic compounds in a number of the samples which are many times higher than the ambient water quality criteria standards. The listing background document has been amended by adding new data giving untreated wastewater pollutant concentrations and the levels of these pollutants in ambient water which may adversely affect aquatic life and human health. (Reference Nos. 18,19,34). We also have reopened the comment period to receive additional comment on this new data. Additionally, if wood preserving plant wastewater did not typically contain significant levels of a number of toxic contaminants, then effluent limitations would not have been placed on this industry under the Clean Water Act.

3. The commenter also objected to the Agency's conclusion that these wastes are uniform throughout the country. The commenter believes that EPA has failed to take into account the various technologies and treatment methods used which would lead to variations in the concentration of the toxic constituents in the wastes. For example, the commenter indicated that sludges generated by evaporation wastewater disposal mechanisms such as cooling towers will contain relatively high concentrations of pentachlorophenol and certain other substances, whereas bottom sediment sludges from biological wastewater treatment lagoons generally contain markedly lower concentrations of pentachlorophenol. The same lack of uniformity also applies to wastewater because of the variations in preservation technologies and wastewater treatment technologies. For example, the commenter indicated that the concentration of pentachlorophenol in wastewater generated in the steam conditioning process, for instance, typically range from 1.2 mg/l to 306 mg/l.\* Therefore, the commenter believes that due to the wide range in the concentrations of the hazardous constituents,

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\* Wood Treating Industry Multimedia Emission Inventory, Corp., June 1980.

wood preserving wastewaters and sludges do not exhibit sufficient uniformity to be listed as hazardous wastes.\*

In responding to this comment, the Agency emphasizes that listing of wood preserving wastewater treatment sludges and wastewaters is justified even if these waste streams have widely varying compositions, provided that wastes meeting this description typically or frequently are hazardous. More extensive review of the concentration levels of the constituents of concern have been included in the revised listing background document. These are contrasted with the concentration levels found to adversely affect aquatic organisms or human health which have been set as ambient water quality criteria levels found in Table 10 of the listing background document (these ambient water quality criteria have recently been signed by the Administrator and are now awaiting Federal Register publication). In all cases, the wastes contained several of the

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\*The commenter also included data in their comments taken from EPA's Background Document for Effluent Limitations, Guidelines and Standards for Timber Products Processing (October 1979) which indicates the concentration of the toxic contaminants in the wastewater to be low. However, this data represents the concentration of these contaminants in the treated effluent wastewater. The Agency believes that this data is inappropriate on which to make a decision on the hazardousness of untreated wastewater.

constituents of concern at concentration levels many orders of magnitude greater than those in Table 10. For example, compare the commenter's low range concentration of 1.2 mg/l pentachlorophenol in untreated wastewater with the concentration of 3.2 ug/l (0.0032 mg/l) which has been found to be acutely or chronically toxic to some freshwater aquatic species. A hypothetical waste concentration of 1 mg/l polynuclear aromatic hydrocarbons should be compared to the ambient water quality criteria of 2.8 ng/l (0.0000028 mg/l) necessary to prevent a human cancer risk of one in  $10^6$ .

Under certain conditions, a concentration of a substance in a waste stream which is greater than the ambient water quality criteria may not present a threat to the environment or to human health. An effluent containing 1 mg/l polynuclear aromatic hydrocarbons could be released to certain remote navigable waters where no significant exposure to humans or aquatic life results. Alternatively, this same waste could potentially be managed in such a way as to significantly affect the quality of the environment and human health by, for example, drinking water contamination on adjacent residential property. We believe the potential causing substantial hazard

is evident, and that hazardous waste regulation therefore is appropriate.

Therefore, the Agency will continue to list these wastes as hazardous because of their extreme toxicities. The Agency believes that the burden should be on the generator to show that their waste is non-hazardous through the de-listing process (§§260.20 and 260.22).

4. The commenter then requested that if the Agency decides to list the wastewater and sludge as hazardous, a minimum cut-off level below which the waste would be considered non-hazardous should be set. The commenter argued that this approach is consistent with the factors for listing wastes as hazardous which are enumerated in Section 261.11(a)(3) and would provide for a more rational basis for regulating the industry. Additionally, the commenter felt that setting a minimum concentration would provide owners and operators of covered facilities with a fixed yardstick to determine whether they produce hazardous wastes and provide significant incentives to fall below the threshold level. As a suggestion, the commenter recommended that the Agency adopt the present effluent limitations of 100 mg/l oil and grease for wood treating wastewater since

EPA's Effluent Guidelines Division has reported that if oil and grease, as measured by Standard Methods is 100 mg/l or less, then pentachloro-phenol and total polynuclear aromatic hydrocarbon concentrations are usually below 15 mg/l and 1 mg/l, respectively.

The Agency agrees with the commenter that setting a minimum cut-off level below which the waste would be considered non-hazardous is desirable; however, the Agency has been unable to do this since no chronic exposure threshold levels, except for those toxic contaminants specified in the National Interim Primary Drinking Water Standards (NIPDWS), relating to drinking water have been established. Additionally, the Agency is concerned with the possibility of volatile emissions from the wastes but again no chronic exposure threshold levels relating to air emission standards have been established. Therefore, the Agency will not set a minimum cut-off level for these wastes, but rather will continue to evaluate the hazardousness of these wastes after considering the factors specified in §261.11(a)(3).

We also note that effluent discharge levels established by the Effluent Guidelines Division

are not necessarily appropriate in evaluating whether a waste is hazardous, since the effluent limitation level is based on the pollutant reduction achieved by Best Available Technology, which standard not only is technology-based, but takes economic considerations into account. The RCRA standard, "may pose a substantial present or potential hazard to human health or the environment when improperly managed" (~~§104~~<sup>0</sup>(5)(B)), is much broader since it is neither technology based, nor are economic considerations relevant. We therefore do not accept the argument that effluent guideline indicator limitation levels should be used to gauge a waste's potential to cause substantial harm if mismanaged.

5. The commenter also indicated that a number of fundamental mistakes were made by the Agency in characterizing these wastes. For example, both benzene and toluene are cited as present in both the wastewater and sludge. With respect to wastewater, the commenter indicates that these constituents are likely to be found only in treating plants which utilize vapor drying, and thus cannot be considered as typical of the industry's wastes. Further, the commenter points out that these substances are likely to be present in only minute quantities.

Moreover, the listing background document contains no evidence that either benzene or toluene are ever present in wood treating wastewater sludge. However, the commenter points out that both benzene and toluene are listed as constituents of concern for the wastewater treatment sludge.

In re-assessing the data, the Agency agrees with the commenter and has revised the listing background document to reflect these changes. Additionally, benzene and toluene have been removed as constituents of concern for both the wastewater and bottom sediment sludges.

6. The commenter also felt that data taken from the California state hazardous waste manifests (i.e., concentration data of pentachlorophenol (5-20%) in the bottom sediment sludge) was inaccurate and refers not to the concentration of pentachlorophenol in the sludge, but rather to the concentration of pentachlorophenol in the original treatment solution. Therefore, the commenter requested that EPA re-examine the accuracy of this data.

In contacting Dr. David Storm of the Department of Health, State of California, the Agency has confirmed the accuracy of this data. We thus will continue to include this data in the listing background document to support the listing of the bottom sediment sludge.

7. The commenter then argued that the listing background document was incorrect in its statement that bottom sediment sludge may accumulate in wastewater treatment ponds for about five years prior to removal (B.D., pp. 153 and 164). The commenter pointed out that sludge from biologically active lagoons may never be removed.

The Agency has amended the listing background document to include this information.

8. The commenter then felt that EPA had severely mischaracterized the biodegradability of pentachlorophenol, i.e., the commenter believes that pentachlorophenol is "readily biodegradable."

The Agency disagrees with the commenter's claim. In data submitted by the commenter, pentachlorophenol in concentrations of 200 ppm or less did not degrade for 205 days. The Agency believes that this period of time is not insignificant, and in fact, is concerned that pentachlorophenol will volatilize into the atmosphere or migrate into groundwater over this time period and will create a substantial hazard to human health and the environment, especially due to the toxicity of pentachlorophenol. The Agency also believes that because of the higher concentrations of pentachlorophenol found in some wood preserving sludges, the biodegradability

of this compound would be less, as discussed in the listing background document. Additionally, pentachlorophenol has been found to persist in warm moist soils for a period of 12 months,\* and also has been detected in human and animal tissues showing that pentachlorophenol in its present ambient environmental concentrations does not degrade readily enough to prevent detectable levels in human and animal tissues.\*\*

The American Wood Preservers Institute itself has acknowledged the difficulty of biodegradation of sludge containing greater concentrations of pentachlorophenol by the following statement:

"While the activated sludge in POTWs has the capacity to biodegrade penta[-chlorophenol], sludge from evaporative disposal mechanisms generally contain high concentrations of wood preserving materials and consequently will not biodegrade unless diluted."\*\*\*

Finally, actual damage incidents have demonstrated the ability of pentachlorophenol and

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\*Harvey, W.A. and A.S. Crafts, 1952, "Toxicity of PCP and its Sodium Salt in Three Yolo Soils", *Hilgardia* 21, 487.

\*\*U.S. EPA, Office of Drinking Water, 1980, Pentachlorophenol Ambient Water Criteria Document.

\*\*\*AWPI, Comments on Timber Products Processing Point Source Category, Feb. 15, 1980.

creosote to persist in the environment for several years. These incidents show empirically that pentachlorophenol can persist in concentrations sufficient to cause substantial harm if mismanaged.

Therefore, the Agency does not consider pentachlorophenol "readily biodegradable" and will continue to include pentachlorophenol as a constituent of concern in the listing of these wastes.

9. The commenter then argued that there is no evidence that tetrachlorodibenzoparadioxin (TCDD) is present as a constituent of wood treating wastewater or bottom sediment sludge as indicated in the listing background document (footnote no. 2, pg. 155).

In re-evaluating the available data, the Agency agrees with the commenter that current data does not indicate the presence of tetrachlorodibenzoparadioxin in the listed wastes except where these wastes are incinerated, since polychlorinated dibenzo-p-dioxins are formed during the incomplete combustion of pentachlorophenol mixtures. Therefore, the listing background document has been modified to reflect this change. Other chlorinated dioxins have been found in commercial pentachlorophenol (Table 4) and could therefore be expected to be present in very small amounts in some wastes.

10. The commenter also argued that EPA's bibliography

is incomplete and often contains only one side of the story on many issues relating to wood preserving. For example, the commenter pointed out that references 15 and 16 are alarmist articles concerning suspected diverse health effects from penta-treated wood while the final report "Miami Epidemiologic Studies Program,"\* which found no correlation with any regulatory used wood preserving chemical and no connection whatsoever with wood treating wastes, was not cited in the listing background document. Additionally, the commenter pointed out that several of the studies relied upon by EPA contain inaccuracies which have not yet been corrected although the Agency has been made aware of these problems.

In preparing the listing background document, the Agency has relied for the most part on data/reports that were available to the Agency. There may have been some studies the Agency was unaware of which were not included in the listing background document. The Agency agrees with the commenter that as much data as possible should be considered

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\*Aldrich, T.E. and R.C. Duncan, "Investigation of Citizen Reported Increase of Cancer Mortality and Morbidity in Madison County, Kentucky in Relation to Pentachlorophenol Exposure," October 24, 1979.

in making a determination on the hazardousness of the waste. Therefore, the Agency has modified the bibliography and will include other studies that are pertinent, including the Miami Epidemiologic Studies Program cited by the commenter.

The Agency would like, however, to make a few comments with respect to this study. The commenter characterized the study as having found no correlation between exposure to regularly used wood preserving chemicals (i.e., pentachlorophenol) and chronic disease. While the Agency believes that this study may not provide the basis for proof of a correlation between exposure to wood treated with pentachlorophenol and chronic disease,\* the Agency does believe it provides enough positive data to be provocative. For example, the study concluded that "[i]n any case, there would appear to be a suggestion of the need for the study of a possible risk between occupational exposure to pentachlorophenol treated materials and leukemia." Additionally, in the November 16, 1979, clarification memorandum included in this study, the statement is made by

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\*Some of the reasons the Agency believes this study does not provide the basis of proof include its limited scope, the inadequate time span allowed from exposure to observation of malignant disease, the possibility that the pentachlorophenol used at the time of exposure contained greater amount of contaminants, etc.

the researchers "[t]hat six (five depot employees and one community) cases from this category [chronic lymphocytic and chronic myelocytic leukemia] would have a common association to pentachlorophenol is remarkable." Therefore, the Agency believes that this study in no way conflicts with the listing background document, or our decision to list pentachlorophenol as a waste constituent of concern.

With respect to the other studies the commenter cites which contain inaccuracies, the Office of Solid Waste has cited data only from those portions of the report which are accurate. Therefore, the Agency believes that it can continue to utilize this data. It should be noted, however, that the Agency expects to correct the inaccuracies in these reports as soon as possible.

11. The commenter also argued that the Agency has failed to cite a single incident of mismanagement of sludge from wood preserving wastewater treatment or wood preserving wastewater which has resulted in any sort of environmental problem. The commenter pointed out that although this criterion is listed as relevant to a hazardous waste listing in §261.11(a)(3)(ix), the absence of any such problems over the history of the wood treating industry does not appear to have received

any attention from EPA. Therefore, the commenter believes that the Agency has failed to adequately assess either the potential for harm from wood preserving wastes or any actual harm which has resulted from sludges from treatment of wood preserving wastewater or the wastewater itself.

The commenter misperceives the regulatory mechanism adopted by the Agency for identifying hazardous waste through the listing process. The factors listed in §261.11(a)(3) need not all be present for a waste to be listed as hazardous. While this factor is relevant in making listing determinations, a waste need not actually have been mismanaged for it to be considered hazardous. In fact, the definition of hazardous waste cited in the Act supports this interpretation, since a waste is hazardous if it "may pose a substantial hazard. . .if improperly managed. . ." Congress thus clearly indicated that damage did not have to be demonstrated before designating a waste as hazardous. If this interpretation was not taken only those wastes which have caused environmental insult could be designated as hazardous. The entire rationale for enacting RCRA, to prevent the mismanagement of hazardous waste and the resulting potential for creating substantial harm to human

health and the environment, would be undermined. Therefore, the Agency believes that actual damage does not have to be demonstrated, but only to show that the waste, if improperly managed, may pose a substantial hazard to human health and the environment which the Agency believes it has done for the two wastes generated from the wood preserving industry.

In any case, we have considered whether these wastes have been involved in damage incidents, and, as shown in the listing background document, mismanagement and actual damage have indeed occurred. We believe these incidents show empirically that these wastes are capable of posing substantial hazard if mismanaged and thus warrant listing.

12. The commenter argued that the Office of Solid Waste has failed to coordinate and take into account the actions of other branches of EPA (i.e., Effluent Guidelines Division and the Special Pesticide Review Division, etc.) with respect to the wood treating industry. More specifically, the commenter believes that the hazardous waste regulations have the potential to overlap or conflict with programs under the Clean Air Act, the Clean Water Act (i.e., regulations to be promulgated on effluent limitations applicable to the wood treating industry) and the Federal

Insecticide, Fungicide and Rodenticide Act (i.e., the RPARs the Agency is currently considering against the three wood preservative chemicals, pentachlorophenol, creosote and the inorganic arsenicals). Therefore, the commenter believes that any regulations promulgated under RCRA must be coordinated with other parts of the Agency to avoid confusion in the regulated community caused by conflicting and environmental programs.

In preparing the listing background document on the wood treating industry (May 2, 1980), the Agency had discussed the various aspects of these listings--wastewater and bottom sediment sludge from the wood treating industry--with other offices within the Agency before promulgating these regulations. Therefore, the Agency did attempt to avoid any internal inconsistencies. However, to ensure that any inconsistencies that still remain are either straightened out or fully explained, the Office of Solid Waste has discussed these listings, along with the comments received by the American Wood Preservers Institute (AWPI), with both the Effluent Guidelines Division and the Special Pesticide Review Division. It should be noted, however, that part of the confusion expressed by the commenter may be due to their misunderstanding of the authorities

and objectives on the various pieces of environmental legislation (e.g., see response to comments nos. 1 and 16 in this background document).

13. The commenter then argued that the quantities of waste generated from wood preserving are not large, and thus do not pose the degree of risk which would warrant subjecting the industry to the burdensome reporting, monitoring, recordkeeping, financial and insurance requirements under Parts 264 and 265. Additionally, the commenter argued that wood preservers do not actually accumulate significant amounts of hazardous waste on-site since their treatment processes renders the waste materials innocuous.

The Agency disagrees with the commenter. Data presented in the listing background document indicates that approximately 200 million gallons of wastewater are generated annually of which approximately 90 percent is treated to generate bottom sediment sludge. Additionally, data provided by the American Wood Preserver's Association indicates generation of total process solid wastes of between 830 to 1530 metric tons/yr, which in the Agency's opinion is a significant quantity of waste, especially in light of the extreme toxicities of the constituents of concern in these particular wastes. Therefore,

the Agency believes that these wastes are generated in sufficient quantity and do pose a risk substantial enough to warrant control under the hazardous waste management control system.

With respect to the commenter's claim that the treatment processes render the waste materials innocuous, the Agency would like to make two points. First, the Act requires that any process which treats a hazardous waste requires a permit under RCRA, thus is subject to control under Subtitle C of RCRA. Second, the Agency believes that insufficient data has been submitted by the commenter to substantiate their claim that these treatment processes render the waste materials (i.e., bottom sediment sludge) innocuous. In this regard, we note that the commenters supplied almost no waste analytic data with their comments, even though the wastes were originally proposed for listing in August, 1979, and even though the July 1980 comment period for comment to the May interim final listing was effectively extended to allow this industry time to gather and present such data. (Industry comments have, however, been helpful and informative in other respects.) Third, information available to the Agency indicates that currently practiced wastewater treatment processes (e.g., cooling/

stripping towers) generate sludges which in the Agency's opinion are not innocuous after consideration of the concentrations of wood preserving oil residues. Indeed, even biological treatment sludges from final retention ponds appear to contain relatively high concentrations of particular waste constituents (see Table 7 to the listing background document).

14. Another commenter argued that three chemicals mentioned in the listing background document (benz[a]anthracene, benzo[b]fluoranthene, and benzo(a)pyrene) are not commonly constituents of "modern" creosote. The commenter further argued that reported adverse effects may have only been caused by certain creosote oils, e.g., those containing benzo[a]pyrene.

The Agency accepts the evaluation conducted by the Carcinogen Assessment Group that creosote itself has substantial evidence of carcinogenicity, and that this propensity derives in part from constituents other than benzo[a]pyrene. Another component of creosote, chrysene, is present in larger quantities (and was listed by the commenter as a constituent even of "modern" creosote) than the three components mentioned by the commenter, and has also been evaluated by EPA's Carcinogen Assessment Group as having substantial evidence of carcinogenicity.

Thus, even if the commenter is correct, we would not alter the waste listing.

But in any case, there is evidence that these compounds are indeed components of creosote. Furthermore, benzo[a]pyrene has been found to be present in creosote by sources other than the commenter.\* It and the other components questioned by the commenter also have been found in both wastewater and bottom sediment sludges from wood preserving plants(18) and has been detected in elevated levels in mussels growing near creosote treated timber pilings (39,40) and in the edible meat of lobsters maintained in commercial tidal compounds constructed of creosote treated timber. (40,41). We thus believe these substances are ordinarily found in creosote and can escape into the environment to cause substantial harm. Therefore, the Agency will continue to include these substances as a basis for listing creosote-containing waste-water and bottom sediment sludges from the wood preserving industry.

15. The commenter argued that pentachlorophenol does not meet RCRA's criteria for classification as an acutely hazardous waste under section 261.11(a)(2),

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\*Guerin, 1977 "Energy Sources of Polycyclic Aromatic Hydrocarbons." Oak Ridge National Laboratory.

and submitted unpublished studies showing that pentachlorophenol had acute toxicity ranges outside of the criteria limits set in section 261.11(a)(2). The commenter asserted that the Department of Transportation (DOT), which uses the same criteria in making determinations of "Poison B" materials responded to the same studies by removing pentachlorophenol from its "Poison B list."\*

First, the Department of Transportation did not consider the toxicity in its delisting of pentachlorophenol. The published rationale for the DOT decision\*\* appears instead to consider only the fact that pentachlorophenol is a solid, instead of a liquid: "This entry is listed with quantity restrictions and packaging requirements for a liquid, yet the material is a solid. . . , it has therefore been deleted because of the uncertainty of entry description." The Agency is not able to acknowledge that the DOT either performed a toxicological validation of the submitted studies or delisted pentachlorophenol for reasons of its correct commercial form.

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\*We note in passing that this comment is actually addressed to the §261.33 regulation. However, since the comment was made in the course of comments on the wood preserving industry waste listing, and pentachlorophenol is of particular significance to this industry, we are responding to the comment here.

\*\*41 FR 40618 (September 20, 1976).

The Office of Pesticides Programs has assisted the Office of Solid Waste by reviewing several published acute toxicity studies on pentachlorophenol. With this validation, the Agency is able to remove pentachlorophenol from the acutely hazardous list. The studies in question are summarized below.

One published study showing an oral lethal dose of 27 mg/kg was performed as a 0.5% solution of pentachlorophenol in fuel oil, and therefore was not found indicative of the toxicity of pentachlorophenol alone without contribution of toxicity from the vehicle. Besides this study, which was criticized by the commenter, the Agency is aware of two additional studies indicating the possibility of an LD<sub>50</sub> value below 50 mg/kg. A recent experiment\* resulted in an oral LD<sub>50</sub> of 36 mg/kg for pentachlorophenol administered to C57 male mice in 40% ethanol. One report estimated the LD<sub>50</sub> for humans to be as low as 29 mg/kg.\*\* The Ahlborg study may also have had toxicity contribution from the vehicle. (This study would not have been available to the DOT for its 1976 decision.) The Dreisbach

\*Ahlborg, U.G., and K. Larsson. "Metabolism of Tetrachlorophenols in the Rat." Arch. Toxicology, 40, 63 (1978).

\*\*Dreisbach, R.H. Handbook of Poisoning, Diagnosis and Treatment, p. 256 (1963).

listing was found too general and without supporting data.

The two unpublished contract studies submitted to the Agency by the commenter were not subjected to validation, since published studies following technically more defensible protocol were available. For example, the material tested by both International BioResearch and Wil Research Laboratories for the commenter is described as "49-162 Pentachlorophenol from Reichhold Chemicals; small brown crystals with a pungent odor." There is no way for the Agency to determine if this substance is technical or purified grade, or if it resembles the commercial products of other companies such as Dow or Monsanto. No analyses of major impurities was given. The crystalline solid tested may have been a product of an isolation/purification synthesis step that never occurs in the preparation of concentrated solutions of pentachlorophenol for major industrial use (technical grade). Also, there exists an inconsistency between the two studies submitted by the commenter in its description of the administered dose. One study describes a 1.0% suspension of the pentachlorophenol in corn oil and the other describes a 50% solution of pentachlorophenol in corn oil. It is highly improbable that identical pentachlorophenol samples would not dissolve in low

concentrations in corn oil, but would dissolve in high concentrations.

16. Finally, the American Wood Preservers Institute has argued both in its comments and in other public forums that the Agency should not promulgate hazardous waste listings for this industry until the Rebuttable Presumption Against Registration (RPAR) process for pentachlorophenol and creosote is completed by the Agency's Office of Pesticide Programs. (The RPAR process is well underway, and is expected to be completed within the next six months.) Indeed, it is suggested that the Agency may be precluded legally from listing these wastes pending completion of RPAR review.

We disagree strongly. The RCRA hazardous waste listing process and the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) cancellation process have different objectives and are governed by different statutory standards. The FIFRA review process balances the environmental hazards with the benefits of use of a pesticide. Thus, under FIFRA, the key determination for registration or cancellation of a pesticide is whether use or continued use "generally causes an unreasonable adverse effect on the environment." (FIFRA Sections 3(d), 6(b).) An 'unreasonable adverse effect on

the environment' is defined as "any unreasonable risk to man or the environment, taking into account the economic, social, and environmental costs and benefits of the use of any pesticide."\* Further, in determining whether to issue a notice of intent to cancel a registration, the Administrator must take into account the proposed action's impact on "production and prices of agricultural commodities, retail food prices, and otherwise on the agricultural economy." (FIFRA Section 6(b).)

No such balancing is involved in making hazardous waste listing determinations (or in identifying hazardous wastes by means of a characteristic) under RCRA. Wastes are to be regulated as hazardous if they are capable of posing a substantial threat to human health or the environment if managed improperly (RCRA Section 1004(5)). No weighing of benefits is mentioned in the statute, nor is such a consideration even germane, since the disposition of solid or hazardous wastes ordinarily has little if any social or economic benefit (see H.R. Rep. No. 94-1491, 94th Cong., 2d Sess. 4 (1976)).

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\*(FIFRA, Section 2(bb), emphasis supplied; see also 40 CFR §162.11(a)(5)(iii) (authorizing consideration in determining whether to cancel a pesticide use of evidence of whether the "economic, social and environmental benefits of the use of the pesticide subject to the presumption outweigh the risk of use."))

Identification and listing of hazardous wastes thus is a significantly different type of determination than RPAR review under FIFRA. Simply put, wastes from manufacture of registered pesticides may well be capable of posing a substantial threat to human health and the environment and thereby be listed as hazardous even if the social, economic and environmental benefits of use of the pesticide outweigh the respective risks and justify its continued registration. This being so, we believe it inadvisable to defer regulation of these wood preserving process wastes pending completion of RPAR review since neither determination controls the other. Indeed, under the integration provision of RCRA (Section 1006(b)), the Agency is to integrate its implementation of RCRA and other environmental statutes (including FIFRA) "only to the extent that it can be done in a manner consistent with the goals and policies expressed in (RCRA) and in the other acts. . ." As shown above, the RCRA listing process and the FIFRA RPAR review process have fundamentally different goals and policies, and fundamentally different substantive statutory standards. We therefore will proceed with our listings of these process wastes.

We note as a further , and central, reason for not deferring regulation that the RPAR process will not consider the composition of wood preserving manufacturing process wastes or their potential to cause substantial harm if mismanaged. These process wastes are not pesticides; nor are they registered for use. Their potential to cause substantial environmental harm if mismanaged is not at issue, or even relevant to the RPAR proceeding. We thus do not accept the advisability, even as a pragmatic matter of deferring RCRA regulation pending completion of RPAR review.

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Key to

BACKGROUND DOCUMENT

RESOURCE CONSERVATION AND RECOVERY ACT

SUBTITLE C - IDENTIFICATION AND LISTING OF HAZARDOUS WASTE

§§261.31 and 261.32 - Listing of Hazardous Wastes (Finalization of May 19, 1980 Hazardous Waste List)

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BACKGROUND DOCUMENT

RESOURCE CONSERVATION AND RECOVERY ACT

SUBTITLE C - IDENTIFICATION AND LISTING OF HAZARDOUS WASTE

§§261.31 and 261.32 - Listing of Hazardous Wastes (Finalization  
of May 19, 1980 Hazardous Waste List)

Received

04-06-81

U.S. ENVIRONMENTAL PROTECTION AGENCY

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## Hazardous Waste Listing Background Document

### INTRODUCTION

Subtitle C of the Solid Waste Disposal Act, as amended by the Resource Conservation and Recovery Act of 1976 creates a comprehensive "cradle-to-grave" management control system for the disposal of hazardous wastes designed to protect the public health and the environment from the improper disposal of such waste. Section 3001 of that Subtitle requires EPA to identify the characteristics of and list hazardous wastes. Wastes identified or listed as hazardous will be included in the management control system created by Sections 3002-3006 and 3010. Wastes not identified or listed will be subject to the requirements for non-hazardous waste imposed by the States under Subtitle D.

### Hazardous Waste List

The purpose of the hazardous waste list as required by Section 3001 of RCRA is to identify those wastes which may present a potential hazard to human health or the environment. The waste so identified is considered hazardous (unless it has been excluded from the list under §§260.20 and 260.22) and subject to the Subtitle C regulations. A solid waste, or class of solid wastes is listed if the waste:

- (1) exhibits any of the characteristics identified in Subpart C of the final regulations; or

- (2) meets the definition of §261.11(a)(2) of the regulations (i.e., may cause or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness) and thus, presents an acute hazard to humans; or
- (3) contains any of the toxic constituents listed in Appendix VIII of Part 261 unless, after considering any of a number of factors, the Administrator concludes that the waste will not meet the criterion of §261.11(a)(3) (i.e., may pose a substantial present or potential hazard to human health or the environment when it is improperly treated, stored, transported, disposed of or otherwise managed).

The Agency considered several approaches for formulating the list. The approaches can be broken down into three main types:

- ° Hazardous Waste from Non-Specific Sources - these are wastes which are generated from a number of different sources (i.e., electroplating, etc.)
- ° Hazardous Waste from Specific Sources - these are wastes which would be generated from a very specific source (i.e., distillation bottoms from the production of acetaldehyde from ethylene, etc.)

- ° Commercial Chemical Products - these are a list of commercial chemical products or manufacturing chemical intermediates which if discarded either as the commercial chemical or manufacturing chemical intermediate itself; off-specification commercial chemical products or manufacturing chemical intermediates; any container or inner liner removed from a container that has been used to hold these commercial chemical products or manufacturing chemical intermediate unless decontaminated; or any residue or contaminated soil, water or other debris resulting from the clean-up of a spill into or on any land or water, of these commercial chemical products or manufacturing chemical intermediates are hazardous wastes.

(This listing background document will cover the first two categories; the third category of hazardous waste is discussed in the background document entitled, "Hazardous Waste from Discarding of Commercial Chemical Products and the Containers and Spill Residues Thereof."

#### HAZARDOUS WASTE FROM NON-SPECIFIC AND SPECIFIC SOURCES

On May 19, 1980, as part of its final and interim final regulations implementing Sections 3001 of RCRA, EPA published

a list of hazardous wastes which included 85 wastes from manufacturing processes (§§261.31 and 261.32, 45 FR 33123-33124). These lists were published in interim final form to allow the public an opportunity to comment on additional data the Agency had collected on these wastes since the close of the initial public comment period on the proposed Subtitle C regulations (43 FR 58957-58959, December 18, 1978).

At the same time, the Agency also proposed for comment eleven additional hazardous waste listings (45 FR 33136-33137, May 19, 1980). All of these wastes were identified by the Agency in the course of developing the necessary technical data to support the May 19, 1980, interim final hazardous waste list.

The background data used to support these listings came primarily from two sources. The majority of this data or information comes from studies undertaken by the Agency or data available to the Agency (i.e., industry assessment studies conducted by the Office of Solid Waste, effluent guidelines studies conducted by the Office of Water Planning and Standards, health effects and fate and transport data compiled by the Office of Research and Development and Office of Water Planning and Standards, damage assessments and incidents compiled by the Office of Solid Waste, etc.)\*.

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\*It should be noted that a number of these documents (e.g., pesticide waste background documents) contain confidential information. This data has been removed from the document and will not be made available to the public. This data, however, is part of the Administrative record and is included in the Agency's case to support the listing.

The second source of data came from information collected from State Agencies (i.e., manifest data, etc.).

The Agency received a large number of comments on both the interim final and proposed hazardous waste listings. We have evaluated these comments carefully and responded in detail in the listing background documents. The respective listing background documents have also been revised as appropriate and are now "final-final" documents.

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CCLC # 201546

**Generic Listings**

## LISTING BACKGROUND DOCUMENT

### Wastes from Usage of Halogenated Hydrocarbon Solvents in Degreasing Operations

The following spent halogenated solvents used in degreasing: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, carbon tetrachloride and the chlorinated fluorocarbons; and sludges from the recovery of these solvents in degreasing operations. (T)\*,\*\*,\*\*\*

#### I. SUMMARY OF BASIS FOR LISTING

Solvent degreasing operations remove grease, wax, dirt, oil, and other undesirable substances from various materials. All degreasing facilities which use the halogenated hydrocarbon solvents listed above generate spent solvent solutions which are either discarded or processed to recover the solvent from the spent solution. Spent solvents include those which are no longer useful without further processing, either because they have outlasted their shelf life or because they have been contaminated, or so changed chemically or physically that they are no longer useful as solvents. The recovery operations invariably generate solvent sludges.

\* In December, 1978, the Agency proposed a generic listing for this class of wastes.

\*\* These solvents are often marketed under various trade marks; the listing obviously includes all trade mark solvents which have the generic chemical name listed above. Another point of consideration is that different names may be used to refer to the same solvent:

tetrachloroethylene = perchloroethylene  
1,1,1-trichloroethane = methyl chloroform  
carbon tetrachloride = tetrachloromethane  
methylene chloride = dichloromethane  
trichloroethylene = 1,1,2-trichloroethylene

\*\*\* In response to industry comments, it should be noted that the Agency is no longer listing these wastes on the basis of ignitability or EP toxicity. However, these solvents may be contaminated with metals (i.e., lead and chromium) in the degreasing operations; therefore, the generator will be responsible for determining whether the waste would also meet the EP toxicity characteristic.

The Administrator has determined that spent halogenated solvents from degreasing and the sludges that result from associated solvent reclamation operations are solid wastes which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of, or otherwise managed; therefore, these wastes should be subject to appropriate management requirements under Subtitle C of RCRA.

For all of the listed waste solvents, this conclusion is based on the following considerations:

1. The chlorinated hydrocarbons are toxic and, in some cases, genetically harmful, while chlorofluorocarbons may deplete the ozone layer following environmental release.
2. Approximately 99,000 metric tons of waste halogenated solvents from degreasing operations are generated each year(1). There are approximately 460,000 facilities dispersed throughout the country that use halogenated solvents and generate these wastes(1). It is estimated that about 30,000 metric tons per year of halogenated hydrocarbons from these facilities are either disposed of annually in landfills or by open-ground dumping, either as crude spent solvents or as sludges. The remainder of these wastes are usually incinerated. The large quantity of wastes generated and the large number of disposal sites utilized increases the possibility of waste mismanagement and environmental release of harmful constituents.
3. Since a large majority of the spent solvents and sludges are in liquid form, the potential for these wastes to migrate from land disposal facilities is high. Further, the solubility of these solvents is generally high, increasing their migratory potential.
4. The spent solvent solution from degreasing operations may contain up to 90 percent of the original solvent. Depending on the recovery technique, sludges that result from reclamation processes can contain up to 50 percent of the original solvent. Such high concentrations

of hazardous constituents increases the chance of waste constituents escaping in harmful concentrations.

5. Spent solvents can create an air pollution problem via the volatilization of the solvents from the wastes.

For the five chlorinated solvents (not including chlorofluorocarbons) found in the waste streams, this conclusion is based on the following considerations:

6. Incomplete combustion of the spent chlorinated hydrocarbon solvents during incineration can cause emissions of the solvent and generate toxic degradation products (e.g. phosgene).
7. These spent halogenated solvents can leach from the waste to adversely affect human health and the environment through the resulting contamination of groundwater.
8. Current waste management practices have resulted in environmental damage. These incidents serve to illustrate that the mismanagement of these wastes does occur and can result in substantial environmental and health hazards.
9. A number of these solvents are carcinogenic or mutagenic, or are suspected carcinogens or mutagens, and are lethally toxic to humans and animals.

For the chlorofluorocarbons, the Agency is basing the listing on the following consideration:

10. Chlorofluorocarbons, after release at the surface of the earth, mix with the atmosphere and rise into the stratosphere where they are decomposed by ultra violet radiation to release chlorine atoms. These atoms catalytically deplete the ozone, leading to adverse effects, including skin cancer and climate changes.

## II. OVERALL DESCRIPTION OF INDUSTRY USAGE

Degreasing operations are not industry specific. Degreasing operations are prevalent in twelve major SIC (Standard Industrial Classification) categories, numerous subcategories, and automotive maintenance shops. The pertinent industries where halogenated hydrocarbons are used primarily are presented in Table 1. A summary of the number and types of plants that conduct degreasing operations is presented in Table 2.

Table 1  
Industries Using Halogenated Hydrocarbons  
in Degreasing Operations

<u>Source</u>	<u>SIC Code</u>
Metal Furniture	25
Primary Metals	33
Fabricated Products	34
Non-electric Machinery	35
Electric Equipment	36
Transportation Equipment	37
Instruments and Clocks	38
Miscellaneous Industry	39
Automotive Repair Shops	75
Automotive Dealers	55
Automotive Maintenance Shops	--
Textile Plants (Fabric Scouring)	22
Gasoline Stations	55

Table 2 - Solvent Degreasing Source Types\*(1)

<u>Source</u>	<u>SIC</u>	<u>Number of Plants</u>	<u>Estimated Number of Vapor Degreasing Operations</u>	<u>Estimated Number of Cold Cleaning Operations</u>
<u>Material Degreasing</u>				
Metal Furniture	25	9,233	492	22,869
Primary Metals	33	6,792	1,547	17,558
Fabricated Products	34	29,525	5,140	76,329
Non-electric Machinery	35	40,792	5,302	105,456
Electric Equipment	36	12,270	6,302	31,720
Transportation Equipment	37	8,802	1,917	22,756
Instruments and Clocks	38	5,983	2,559	15,467
Miscellaneous	39	15,187	886	39,262
<u>Automotive</u>				
Auto Repair Shops	75	127,203		141,977
Automotive Dealers	55	121,369		135,463
Gasoline Stations	55	226,445		277,440
Maintenance Shops		320,701		252,735
<u>Textiles</u>				
Textile Plants (Fabric Scouring)	22	<u>7,201</u>		
<b>Total</b>		<b>931,513</b>	<b>24,145</b>	<b>1,230,006</b>

\*Includes facilities which do not use halogenated solvents

III. OVERALL PROCESS DESCRIPTION, WASTE GENERATION LEVELS  
AND GEOGRAPHIC DISTRIBUTION OF DEGREASING FACILITIES

1. Solvents Used in Degreasing Process

As indicated in Table 3, out of the more than 1,230,000 non-halogenated and halogenated degreasing operations (see Table 2), approximately 460,000 use halogenated solvents(1). Table 3 breaks down the number of plants which use halogenated solvents to show the estimated number of these plants using a particular halogenated solvent by their type of degreasing operation. As the table indicates, the largest number of these plants use cold cleaning and open top vapor degreasing operations (see next section for more detailed discussion of specific degreasing operations). In both of these operations, the largest number use trichloroethylene and trichlorethane. Of the industries with conveyORIZED vapor degreasing operations, the largest number use trichloroethylene; fabric scouring operations use principally tetrachloroethylene (perchloroethylene). Overall, trichloroethylene is the solvent used most prevalently.

2. Process Description

Degreasing operations may be classified into four basic categories: cold cleaning, vapor degreasing (open top), vapor degreasing (conveyORIZED), and fabric scouring.

In cold cleaning operations, the solvent is maintained well below its boiling point. The item to be cleaned is either immersed in the agitated solvent

Table 3 - Estimated Number of Plants using Halogenated  
Solvents by Type of Degreasing (1974) (1)

Solvent	Vapor (open top)	Cold Cleaning	Vapor Conveyorized	Fabric Scouring
Carbon tetrachloride		10,568		
Fluorocarbons*	2,130	66,932	319	
Methylene Chloride	298	21,136	45	
Tetrachloroethylene	3,121	45,795	467	2,522
Trichloroethylene	11,440	149,715	1,713	693
Trichloroethane	<u>4,011</u>	<u>137,386</u>	<u>601</u>	<u>        </u>
Total	21,000	431,532	3,145	3,215

Note: Blanks indicate no use of specified solvent in that type of degreasing operation.

\*This refers to all fluorocarbons, some of which are chlorinated.

or suspended above the solvent where it is systematically sprayed in a manner similar to that of an automatic dish washer. Simple cold cleaning operations may even consist of a container of solvent in which items are manually immersed, as is the case in small auto repair shops and in service stations.

Simple vapor degreasing (open top) is achieved by suspending the item to be cleaned above the boiling solvent in a vat. Condensation continues until the temperature of the object approaches that of the solvent vapors. Often the suspended item is sprayed with liquid solvent to facilitate further degreasing. In order to control vapor emissions, a layer of cold air is often maintained above the open top degreaser.

The conveyORIZED vapor degreaser operates in much the same manner, except that the objects to be cleaned are continuously conveyed through the vapor zone. Auxiliary solvent sprays are also used to improve the cleaning efficiency of the operations.

Fabric scouring operations are slightly more complex. Generally, the fabric is conveyed through the degreasing machine, where it is sprayed with solvents. The solvents are then removed with an aqueous solution of alcohol.

### 3. Waste Generation Levels and Projected Levels

The annual growth rate for the use of the listed halogenated solvents in degreasing applications is expected to

be 4 percent(1). Growth is expected to be uniform among the various solvents, except for trichloroethylene, which has been banned in several states for use in occupational settings because it is a carcinogen. (1,2,21). In California, the use of trichloroethylene has been restricted by legislation, but tetrachloroethylene and 1,1,1-trichloroethane are exempt(1) from the restrictions and are still used in degreasing operations. Rhode Island has completely banned the use of trichloroethylene(2).

#### 4. Geographic Distribution of Degreasing Operations

The location of the vapor degreasing operations has been determined by identifying the industries with which the operations are associated. There are about 24,145 vapor degreasing operations in the United States, which consume about 52 percent of the total halogenated solvents used(1). More than 63 percent of these operations are found in nine states (California, Illinois, Massachusetts, Michigan, New Jersey, New York, Ohio, Pennsylvania and Texas). Figure 1 and the associated Table 4 present the geographic distribution of these plants.

There are about 431,532 operations that perform cold cleaning using about 35 percent of the total halogenated solvent consumption, while approximately 3,125 fabric scouring operations consume about 13 percent of the total halogenated solvent(1). Assuming an equal distribution of halogenated solvent use among cold cleaning and fabric scouring operations, over 59 percent

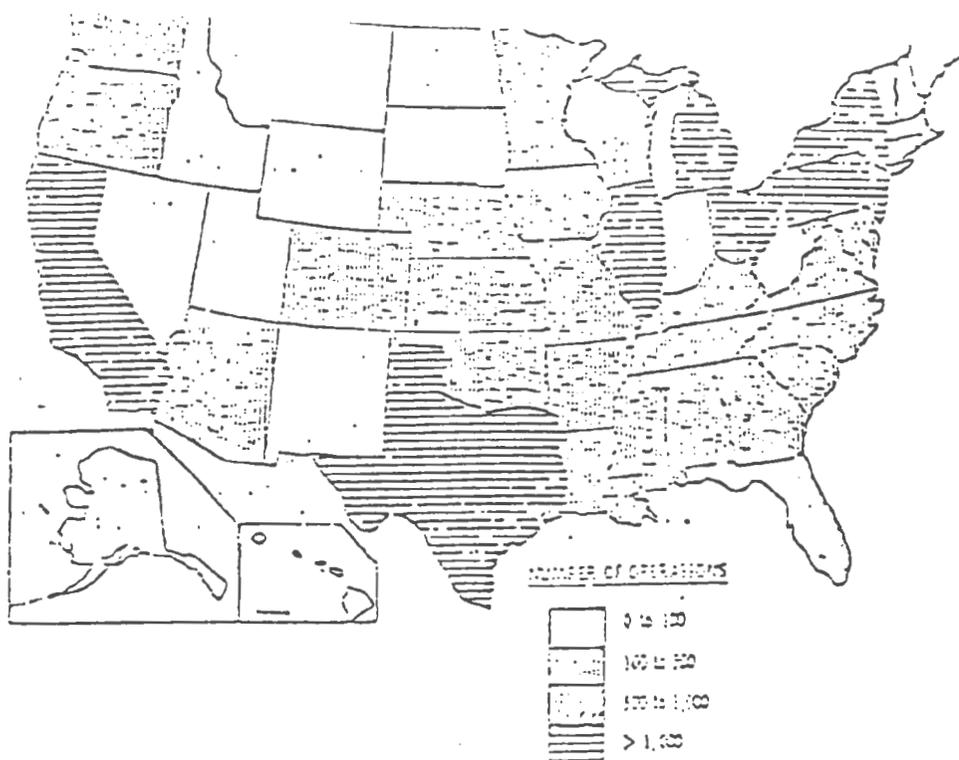


Figure 1 - GEOGRAPHIC DISTRIBUTION OF VAPOR DEGREASING OPERATIONS (1)

Table 4 - GEOGRAPHIC DISTRIBUTION OF VAPOR (OPEN TOP AND CONVEYORIZED) DEGREASING OPERATIONS (1).

State	Number of plants	State	Number of plants
Alabama	247	Montana	25
Alaska	0	Nebraska	102
Arizona	169	Nevada	30
Arkansas	147	New Hampshire	35
California	3,313	New Jersey	1,300
Colorado	219	New Mexico	54
Connecticut	646	New York	2,514
Delaware	29	North Carolina	407
District of Columbia	11	North Dakota	20
Florida	730	Ohio	1,575
Georgia	315	Oklahoma	255
Hawaii	29	Oregon	246
Idaho	39	Pennsylvania	1,146
Illinois	1,737	Rhode Island	121
Indiana	688	South Carolina	143
Iowa	225	South Dakota	25
Kansas	217	Tennessee	356
Kentucky	193	Texas	1,119
Louisiana	174	Utah	69
Maine	45	Vermont	39
Maryland	237	Virginia	218
Massachusetts	523	Washington	314
Michigan	1,836	West Virginia	28
Minnesota	426	Wisconsin	404
Mississippi	116	Wyoming	7
Missouri	459		
		Total	14,145

of the total halogenated solvent used for degreasing occurs in ten states (California, Illinois, Massachusetts, Michigan, New Jersey, New York, Ohio, Pennsylvania, Texas and North Carolina).

#### IV. WASTE STREAM SOURCES AND DESCRIPTION

The usefulness of a solvent decreases with time as contaminants adulterate and become concentrated in the solvent. When the boiling point of the solution (i.e., solvent and contaminants) increases to about 30°C above that of the pure solvent, the solvent is considered spent. Halogenated solvent use pattern by type of degreasing operation is presented in Table 5. Approximately 527,520 metric tons of halogenated solvents are used each year for degreasing operations(1).

Spent solvent solutions include those solvents which are no longer useful without further processing, either because they have outlasted their shelf life or because they have been contaminated, or so changed chemically or physically that they are no longer useful as solvents. These spent solvents are either disposed of, reclaimed and recycled by the waste generator, or processed by a contract solvent reclaiming operator.\* Reclamation is achieved via settling and/or batch distillation. The listed sludge results from this reclamation process.

The composition of the spent solvent is dependent on the application of the degreasing operation. The spent solvent

\*At this time, applicable requirements of Parts 262 through 265 and 122 will apply insofar as the accumulation, storage and transportation of hazardous wastes that are used, reused, recycled or reclaimed. The Agency believes this regulatory coverage is appropriate for the subject wastes. These wastes are hazardous insofar as they are being accumulated, stored or transported. These wastes may not pose a substantial hazard during their recycling and, even though its listed as hazardous, this aspect of their management is not presently being regulated.

Table 5

USE PATEERN OF HALOGENATED SOLVENTS IN DEGREASING AND  
FABRIC SCOURING OPERATIONS IN 1974

Chemical	Total U.S. Consumption (10 <sup>3</sup> kkg)	U.S. Consumption for Degreasing (10 <sup>3</sup> kkg)		U.S. Consumption for Fabric Scouring (10 <sup>3</sup> kkg)	Total U.S. Consumption for Degreas and Scourin (10 <sup>3</sup> kkg)
		Cold	Vapor		
Halogenated hydrocarbons:					
Carbon tetrachloride	534.8	0.72	5		5.72
Fluorocarbons*	428.6	6	11.1		17.1
Methylene Chloride	235.4	46.2	10		56.2
Perchloroethylene	330.2	11.4	43	54.6	109
Trichloroethylene	173.7	43.8	112.7	15	171.5
Trichloroethane	236.3	78	90		<u>168</u>
TOTAL	1939.0	186.12	271.8	69.6	527.52

\*This refers to all fluorocarbons, a percentage of which are chlorinated.

solution contains up to 90 percent of the original solvent(4). Depending on the recovery technique, sludges which result from reclamation processes contain from 1 to 50 percent of the original hydrocarbon solvent(5). However, because of the economic considerations of the reclaiming process, the solvent content of the sludge is seldom reduced below 10 percent. Heavy metal fines and other organics are also present in these wastes, in addition to the original solvent(3).

#### V. QUANTITIES OF THE WASTE AND TYPICAL DISPOSAL PRACTICES

Disposal practices include overt open ground dumping, containerized landfilling, and incineration (3). Approximately 99,000 metric tons of waste halogenated solvents from degreasing operations are generated annually(1). It is estimated that about 30,000 metric tons of these are either landfilled or open dumped. The remaining quantity of waste halogenated solvents from degreasing operations are incinerated. The rationale and derivation of this estimated quantity is presented in Appendix I.

#### VI. HAZARDOUS PROPERTIES OF THE WASTES

As indicated earlier, the spent halogenated solvents and sludges from the reclamation of these solvents contain very significant concentrations of the solvent itself -- the spent solvent solution contains up to 90 percent of the original solvent and the sludge contains a minimum of 10 percent of the original solvent. The landfilling or open ground dumping of these wastes in an unsecure land disposal facility may

result in the migration of the toxic halogenated solvents into the surrounding environment, thus becoming a potential contaminant of groundwater. For example, since a large majority of these wastes are in liquid form -- including all of the spent solvents -- these wastes' physical form makes them amenable to migration from a land disposal facility. Additionally, the solubility in water of these halogenated solvents is appreciable (13): 1,1,1-trichloroethane - 950 mg/l, tetrachloroethylene 150 mg/l, methylene chloride - 20,000 mg/l, carbon tetrachloride 800 mg/l, and trichloroethylene - 1,000 mg/l(14a). These relatively high solubilities demonstrate a strong potential for migration of these substances from inadequate land disposal facilities in substantial concentrations. Thus, improperly constructed or managed landfills (for example, landfills located in areas with permeable soils, or landfills with inadequate leachate control practices) could easily fail to impede leachate formation and migration. Haphazard dumping of the wastes is even more likely to result in migration of waste constituents.

Once released from the matrix of the waste, the halogenated solvents could migrate through the soil to ground and surface waters utilized as drinking water. In the National Organics Monitoring Survey, the Agency detected a number of these solvents in drinking water samples tested over the past several years, thus demonstrating the propensity of these solvents to migrate from the

waste disposal environment and to persist in drinking water following migration\* (14a, 14b, 14c, 14e). In addition, a number of actual documented damage incidents show the potential for a very common halogenated solvent, trichloroethylene, to leach from disposal sites into groundwater. (See Damage Incidents Resulting from the Mismanagement of Halogenated Hydrocarbons, p. 16.)

These actual damage incidents confirm literature data points indicating the environmental persistence of these compounds. Thus, 1,1,1-trichloroethane, methylene chloride, and carbon tetrachloride are all likely to persist in the environment long enough to reach environmental receptors (1,1,1-trichloroethane is subject to hydrolysis, but has a half-life in groundwater of 6 months)(37).

Another problem which could result from improper landfilling of these wastes is the potential for the contaminants to volatilize into the surrounding atmosphere. All of the listed chlorinated solvents are volatile and thus could present an air pollution problem if they are improperly managed (for example, disposed of in the open, or without adequate cover), since they are uniformly toxic via inhalation.

A special problem is posed by chlorofluorocarbon solvents. These solvents are also highly volatile, but instead of posing a direct toxicity hazard, they may be released at the surface of the earth, mix with the atmosphere and rise slowly into the stratosphere,

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\*The specific solvents detected in these samples were methylene chloride, carbon tetrachloride, trichloroethylene, and tetrachloroethylene and trichlorofluoromethane.

Damage Incidents Resulting From The Mismanagement of  
Trichloroethylene

1. In one incident in Michigan, an automotive parts manufacturing plant routinely dumped spent degreasing solutions on the open ground at a rate of about 1000 gallons per year from 1968 to 1972. Trichloroethylene was one of the degreasing solvents present in the spent solutions. Beginning in 1973, trichloroethylene was detected at levels up to 20 mg/l in nearby residential wells. The dump site was the only apparent source of possible contamination (10).
2. In a second incident, also in Michigan, an underground storage tank leaked trichloroethylene which was detected in local groundwater up to four miles away from the land (11).
3. In April of 1974, a private water well in Bay City, Michigan became contaminated by trichloroethylene. The only nearby source of this chemical was the Thomas Company (which replaced the well with a new one). The company claimed that, although it had discharged trichloroethylene into the ground in the past, it had not done so since 1968. Nevertheless, in May of 1975, two more wells were reported to be contaminated with trichloroethylene at concentrations of 20 mg/l and 3 mg/l, respectively (12).

In March, 1978, EPA banned the use of chlorofluorocarbons in aerosol propellants. The primary concern in the enactment of this ban was the ozone depletion effects resulting from chlorofluorocarbons entering the stratosphere and reaction with ozone. In the troposphere, chlorofluorocarbons are decomposed by the intense ultra violet radiation to release chlorine atoms. The chlorine atoms catalytically remove ozone, thereby reducing the total amount of ozone in the stratosphere, leading to an increase in skin cancer, climatic changes and other adverse effects.(33,34) The Agency is therefore concerned about chlorofluorocarbon use and disposal. Therefore, the Agency has proposed the regulation of non-aerosol uses of chlorofluorocarbons.(8)

The Agency also expects to propose regulations controlling the airborne emissions of these solvents and other volatile organics so as to reduce the air pollution problems presented when these solvents are used or disposed. These proposed regulations will apply certain standards to a number of the Volatile Organic Compounds (VOC) which have been demonstrated to be precursors of or lead to the formation of ozone and other photochemical oxidants in the atmosphere. Ozone air pollution endangers the public health and welfare and is thus reflected in the Administrator's promulgation of a National Ambient Air Quality Standard for Ozone (February 8, 1979, 44 FR 8202). Additionally, 1,1,1-trichloroethane and

methylene chloride, which are not ozone precursors, are being regulated under the proposed rule since under EPA's proposed airborne carcinogen policy, a compound which shows evidence of human carcinogenicity is a candidate for regulation under Section 111 as a pollutant "reasonably anticipated to endanger public health and welfare". Finally, trichlorofluoromethane, as indicated in the earlier discussion of chlorofluorocarbons in general, has been implicated in the depletion of the stratospheric ozone layer, a region of the upper atmosphere which shields the earth from harmful wavelengths of ultra violet radiation, that would increase skin cancer risks in humans. (33,34)

Additionally, if these wastes are incinerated, as a large percentage are, and the wastes are not subject to proper incineration conditions (i.e., temperature and residence times), pollution of the environment may result from the airborne disposal of uncombusted halogenated organics, partially combusted organics and newly formed organic compounds. Phosgene is an example of a partially combusted chlorinated organic which is produced by the decomposition or combustion of chlorinated organics by heat(15,16,17). Phosgene has been used as a chemical warfare agent and is recognized as extremely toxic.

The large quantities of the spent solvent and sludges resulting from the recovery of these solvents, a combined total of 99,000 metric tons per year, are another area of concern.

As previously indicated, these wastes are generated in substantial quantities and contain very high concentrations of the original solvent (the spent solvent solution contains up to 90 percent and the sludges contain up to 50 percent of the original solvent). The large quantities of these contaminants pose the danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time, since large amounts of pollutants are available for environmental loading. All of these considerations increase the possibility of exposure to the harmful constituents in the wastes.

VII. HEALTH AND ECOLOGICAL EFFECTS ASSOCIATED WITH THE CONSTITUENTS IN THE WASTES

The toxicity of tetrachloroethylene, methylene chloride, 1,1,1-trichloroethane, trichloroethylene, carbon tetrachloride and chlorofluorocarbons has been well documented. Capsule descriptions of the adverse health and environmental effects are summarized below; more detail on the adverse effects of these solvents can be found in Appendix A.

Tetrachloroethylene has been included on EPA's list of chemicals which have demonstrated substantial evidence of carcinogenicity.(21) Repeated exposure of rats and mice to tetrachloroethylene in air or in the diet has resulted in fatty degeneration of the liver, increased kidney weight and toxic nephropathy.(18,19,20). Additionally, tetrachloroethylene is slightly toxic to freshwater fish.(14b,22,23)

Methylene chloride has been shown to be mutagenic to a bacterial strain, *S. typhimurium*.(24) In addition, acute exposure to methylene chloride in humans is a central nervous system depressant resulting in narcosis in high concentrations and is metabolized to carbon monoxide and causes an increase in carboxyhemoglobin(25).

Although 1,1,1-trichloroethane (MC) has been shown in an NCI bioassay to induce a variety of neoplasms(26), these data were not conclusive. A high incidence of deaths in test animals has led to retesting of this compound by a manufacturer and the NCI(26). In vitro studies have indicated that MC is slightly mutagenic in the Ames test, and can cause mammalian cell transformation. Human toxic effects seen after exposure to 1,1,1-trichloroethane include changes in several central nervous system functions, including reaction time, perceptual speed, manual dexterity and equilibrium(27). In addition, animal studies have produced toxic effects in the central nervous system, cardiovascular system, pulmonary system, and induced liver and kidney damage(27).

Trichloroethylene has been included on EPA's list of chemicals which have demonstrated substantial evidence of carcinogenicity.(21) Trichloroethylene has also been shown, both through acute and chronic exposure, to produce disturbances of the central nervous system and other neurological effects(28,29,30).

Carbon tetrachloride has been included on EPA's list of chemicals which have demonstrated substantial evidence of

carcinogenicity.(21) In addition, toxicological data for non-human mammals are extensive and show carbon tetrachloride to cause liver and kidney damage, biochemical changes in liver function and neurological damage(32).

The hazards associated with exposure to the above halogenated solvents have been recognized by other regulatory programs. Tetrachloroethylene, methylene chloride, 1,1,1-trichloroethane, trichloroethylene, and carbon tetrachloride and the two fluorocarbons, trichlorofluoromethane and dichlorodifluoromethane, are listed as toxic pollutants in accordance with §307(a) of the Clean Water Act of 1977.\* Under §6 of the Occupational Safety and Health act of 1970, final standards for occupational exposure have been established and promulgated in 29 CFR 1910.1000 for carbon tetrachloride, methylene chloride and 1,1,1-trichloroethane. On March 17, 1979, fully halogenated fluorocarbons were banned by the Consumer Products Safety Commission as propellants in the United States, except for essential uses because of their threat to the ozone. In addition, final or proposed regulations in the States of California, Louisiana, Maryland, Massachusetts, Minnesota, Missouri, New Mexico, Oklahoma and Vermont define compounds containing one or more of the solvents tetrachloroethylene, methylene chloride, 1,1,1-trichloroethane, trichloroethylene, carbon tetrachloride and trichlorofluoromethane as hazardous wastes or components thereof.35

\*The Agency has recently proposed to remove trichlorofluoromethane and dichlorodifluoromethane from the list of toxic pollutants under §307(a) of the Clean Water Act (45 FR 46103, July 9, 1980).

## ATTACHMENT I

### DERIVATION OF THE ESTIMATED QUANTITIES OF THE WASTE

#### I. ANNUAL QUANTITIES OF WASTES

Total amount of spent solvents (Halogenated and non-halogenated)<sup>(1)</sup> = 425,560 kkg

Total amount of spent solvents from vapor degreasing<sup>(1)</sup>  
= 54,560 kkg

Vapor degreasing units only use halogenated solvents so all of the 54,560 kkg from this source are halogenated solvents. Cold cleaners and fabric scourers use both halogenated and non-halogenated solvents. Assume that the spent solvent solutions contain solvents in the same proportion as their use. About 12 percent of solvent use in applications other than vapor degreasing is halogenated<sup>(1)</sup>.

∴ (425,560 kkg - 54,560 kkg) (0.12)<sup>(1)</sup>  
= 44,250 kkg of halogenated solvents contained in wastes  
from sources other than vapor degreasing

54,560 kkg + 44,520 kkg = 99,000 kkg of halogenated  
solvents yr

#### II. DISPOSITION OF WASTE

The disposition of about 30 percent of these wastes can be derived from information which is documented in the literature. The disposition of the remaining 70 percent is based upon extrapolations and economic consideration of waste management alternatives.

##### A. DISPOSITION OF 30 PERCENT OF THE WASTE

- ° Vapor degreasers only use halogenated solvents<sup>(1)</sup>
- ° Virtually all metal finishing shops (SIC 35, 36, 37, and 39), and by implication vapor degreasing operations, either reclaim their spent solvents or sell them to solvent refiners.<sup>(1,3)</sup>
- ° Between 50-99 percent of the solution is recovered<sup>(4,5)</sup>
- ° Approximately 37 percent of the plants which recover these solvents on-site dispose of their waste sludges in landfills<sup>(3)</sup>.

(amount of waste) (1-percent recovery)(percent of plants with on-site recovery) x (percent of plants that landfill) = Amount of waste landfilled.

1. Assume 50 percent of the solution is recovered

$$(54,560 \text{ kkg}) (0.50)(0.37)(0.70) = 7,065 \text{ kkg}$$

2. Assume 99 percent of the solution is recovered

$$(54,560 \text{ kkg}) (0.01) (0.37)(0.70) = 140 \text{ kkg}$$

140 kkg to 7,065 kkg of halogenated solvents disposed of in landfills.

About 20 percent of the solvent reclaimers which process the remaining 63 percent of the solvents from this source also landfill their waste. The remaining 80 percent of the solvent reclaimers reportedly incinerate their sludges(4,5). Therefore an additional 109 to 5,456 kkg of halogenated solvents are landfilled by solvent reclaimers.

#### B. DISPOSITION OF THE REMAINING 70 PERCENT OF THE WASTE

The wastes generated by the plants in the SIC categories delineated above represent about 60 percent of all vapor degreasing operations and about 30 percent of all wastes generated by all degreasers. Reportedly, a facility which generates at least 350 gallons of spent halogenated solvents annually has economic incentive to implement a recovery strategy(4,9). Virtually all vapor degreasers meet this criteria.

The disposition of spent solutions from cold cleaning and fabric scouring operations is not as well defined. In order to account for these wastes, some economic factors have been considered. In general, it is expected that a plant or industry which has a high incidence of use of a relatively expensive solvent will probably have some kind of recovery strategy, assuming the scale of operations permits an acceptable payback period. In cold cleaning and fabric scouring operations, the following factors are pertinent:

- ° Cold cleaning and fabric scourers use halogenated solvents in conjunction with inexpensive non-halogenated solvents. It has been estimated that these operations must have six to twelve times the solvent throughput of plants which only use halogenated solvents in order to economically justify a recovery strategy.
- ° Cold cleaning and fabric scouring operations represent about 94.7 percent of all facilities that use halogenated solvents but only use about 48 percent of the total supply of these solvents

that are used for degreasing. The implication is that, on the average, the solvent throughput rate is much lower in this segment of the degreasing industry than that of the vapor degreasing segment.

Although some cold cleaning and fabric scouring operations probably operate on a scale that would make a recovery strategy economically attractive, it is not possible to estimate the extent of recovery operations in this segment of the industry. The economics seem to indicate that the incidence of recovery from these operations is probably very low.

C. THE GROSS ESTIMATE

In estimating the disposition of all the wastes, the best and worst cases pertaining to the portion of the waste which cannot be documented in the literature are considered. The ideal case is where all of the wastes from cold cleaning and fabric scouring operations are processed by contract reclaimer using maximum efficiency recovery techniques (i.e., 99 percent recovery). The worst case would be where all of this waste is simply disposed of. The following is the basis for the estimate.

From Section A

249 kkg to 12,521 kkg of halogenated solvents are landfilled.

Best Case for Cold Cleaning and Fabric Scouring

(amount of waste)(percent recovered)(percent landfilled) = amount landfilled

(44,520 kkg)(0.01)(0.2) = 90 kkg of waste landfilled

Worst case for cold cleaning and fabric scouring is when all 44,520 kkg of waste is landfilled

The estimated best and worst cases for the disposition of halogenated solvents from all types of degreasing operations are 339-57,041 metric tons per year. It is unlikely that either the best or worst case is representative of reality. In this case, about half of the waste is generated by vapor degreasers where it is likely that the incidence of recovery is high. The remaining half is generated in environments where

the incidence of recovery is probably very low. A reasonable inference and prudent estimate based on available data would be about 30,000 metric tons per year of halogenated solvents disposed of on land.

## REFERENCES

1. Hoogheem, T.J., et al. Source assessment: Solvent evaporation degreasing operations. U.S. EPA No. 600/12-79-019f. NTIS PB No. 80 128 812. August, 1979.
2. Mansville Chemical Products. Chemical products synopsis: trichloroethylene. Mansville, New York. September, 1976.
3. U.S. EPA. Hallowell, J.B., et al. Assessment of industrial hazardous waste practices: Electroplating and metal finishing industries - job shops. U.S. EPA. NTIS PB No. 264 349. September, 1976.
4. U.S. EPA. Organic solvent cleaners-background information for proposed standards. U.S. EPA No. 450/2-78-045a. October, 1979.
5. U.S. EPA. Source assessment: Reclaiming of waste solvents. State of the art. NTIS No. 282 934. April, 1978.
6. Not used in text.
7. Not used in text.
8. Federal Register, Vol. 43, Pg. 11301. March 17, 1978.
9. U.S. EPA. Control of volatile organic emissions from solvent metal cleaning. U.S. EPA No. 450/2-77-022. November, 1977.
10. Michigan Department of Natural Resources - Geological Survey Division. Case history #48.
11. Shellenbarger, P. New charge hits Air Force. The Detroit News. May 17, 1979.
12. U.S. EPA. Open files. Hazardous Site Control Branch, WH-548, U.S. EPA, 401 M St., S.W., Washington, DC. 20460. Contact Hugh Kauffman. (202) 245-3051.
13. U.S. EPA. Section II of Appendix B of the listing background document: Fate and transport potential of the hazardous constituents. U.S. EPA, Office of Solid Waste. 1980.
- 14a. U.S. EPA. Trichloroethylene: Ambient water quality criteria. NTIS PB No. 292 443. 1979.
- 14b. U.S. EPA. In-depth studies on health and environmental impacts of selected water pollutants. Work resulting from Contract No. 68-01-4646. 1978.

- 14c. U.S. EPA. Preliminary assessment of suspected carcinogens in drinking water, and appendices. A report to Congress. Washington, D.C. EPA No. 560-4-75-003. 1975.
- 14d. Not used in text.
- 14e. U.S. EPA. The National organic monitoring survey. Technical Support Division, Office of Water Supply, U.S. EPA. Washington, DC. 20460. 1978.
15. Edwards, John B. Combustion formation and emission of trace species. Ann Arbor Science. 1977.
16. NIOSH criteria for recommended standard: Occupational exposure to phosgene. HEW, PHS, CDC, NIOSH. NTIS PB 267 514. 1976.
17. Chemical and Process Technology Encyclopedia. McGraw Hill. 1974.
18. National Cancer Institute. Bioassay of tetrachloroethylene for possible carcinogenicity. NTIS PB No. 272 940. NCI-CG-TR-13. DHEW Publication No. (NIH) 77-813. 1977.
19. Rowe, V.K., et al. Vapor toxicity of tetrachloroethylene for laboratory animals and human subjects. AMA Arch. Ind. Hyg. Occup. Med. 5:566. 1952.
20. Klaassen, C.D., and G.L. Plaa. Relative effects of chlorinated hydrocarbons on liver and kidney function in dogs. Toxicol. Appl. Pharmacol. 10:119. 1967.
21. U.S. EPA. Carcinogen Assessment Group, Office of Research and Development. List of carcinogens. April 22, 1980.
22. Alexander, H., et al. Toxicity of perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, and methylene chloride to fathead minnows. Bull. Environ. Contam. Toxicol. 20:344. 1978.
23. U.S. EPA. Tetrachloroethylene: Ambient water quality criteria. NTIS PB No. 292 445. 1979.
24. Simmon, V.F., et al. Mutagenic activity of chemicals identified in drinking water. S. Scott, et al., eds. In: Progress in genetic toxicology. 1977.
25. National Academy of Sciences. Chloroform, carbon tetrachloride and other halomethanes: Environmental assessment. Publication No. 2763. 1978.

26. National Cancer Institute. Bioassay of 1,1,1-trichloroethane for possible carcinogenicity. NCI-CG-TR-3. NTIS PB No. 265 082. 1977.
27. U.S. EPA. Chlorinated ethanes: Ambient water quality criteria. NTIS PB No. 297 920. 1979.
28. Nomiyama, K., and H. Nomiyama. Metabolism of trichloroethylene in human sex differences in urinary excretion of trichloroacetic acid and trichloroethanol. Int. Arch. Arbeitsmed. 28:37. 1971.
29. Bardodej, A., and J. Vyskocil. The problem of trichloroethylene in occupational medicine. AMA Arch. Ind. Health. 13:581. 1956.
30. McBirney, B.S. Trichloroethylene and dichloroethylene poisoning. AMA Arch. Ind. Hyg. 10:130. 1954.
31. Not used in text.
32. Von Oettingen, W.F. The halogenated hydrocarbon of industrial and toxicological importance. In: Elsevier monographs on toxic agents. E. Browning, ed. Elsevier Publishing Company. New York. 1964.
33. National Academy of Sciences, National Research Council. Halocarbons: Environmental effects of chloromethane release. Publication No. 2529. 1976.
34. National Academy of Sciences, National Research Council. Committee on Impacts of Stratospheric Change. Stratospheric ozone depletion by halocarbons: Chemistry and transport. 1979.
35. U.S. EPA. State Regulations Files. Hazardous Waste Programs, WH-563, U.S. EPA., 401 M St., S.W., Washington, DC. 20460. Contact Sam Morekas. (202) 755-9145.
36. Not used in text.
37. Dawson, English and Petty. Physical chemical properties of hazardous waste constituents. 1980.

WASTES FROM USAGE OF ORGANIC SOLVENTS

I. LISTING

The listed wastes are those major streams which result from usage of organic solvents. The listed solvents include both halogenated and non-halogenated organic compounds. The specific wastes listed are:

The following spent halogenated solvents: tetrachloroethylene, methylene chloride, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene, 1,1,2-trichloro-1,2,2-trifluoroethane, o-dichlorobenzene, trichlorofluoromethane, and the still bottoms from the recovery of these solvents (T);

The following spent non-halogenated solvents: xylene, acetone, ethyl acetate, ethyl benzene, ethyl ether, n-butyl alcohol, cyclohexanone, methanol, methyl isobutyl ketone; and the still bottoms from the recovery of these solvents (I);

The following spent non-halogenated solvents: cresols and cresylic acid, and nitrobenzene; and the still bottoms from the recovery of these solvents (T); and

The following spent non-halogenated solvents: toluene, methyl ethyl ketone, carbon disulfide, isobutanol, pyridine; and the still bottoms from the recovery of these solvents (I,T).

Listing codes for the most widely used halogenated organic solvents are presented in Table I-1, and codes for widely-used non-halogenated organic solvents are in Table I-2.

II. SUMMARY OF BASIS FOR LISTING

Wastes resulting from usage of organic solvents typically contain significant concentrations of the solvent. Examples of wastes from usage of organic solvents include still-bottoms

from solvent recovery and spent solvents from dry cleaning operations and maintenance and repair shops.

The Administrator has determined that waste from usage of the 24 organic solvents listed in Tables I-1 and I-2 may be a solid waste, and as a solid waste, may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations\*:

1. Of the list of 24 solvent types presented in Tables I-1 and I-2, each solvent exhibits one or more properties (i.e., ignitability and/or toxicity) which pose a potential hazard. These solvents represent approximately 95 percent or more of organic solvent usage in the United States (see Table II-1).
2. The use of organic solvents is widespread throughout the United States, and the quantities involved are large; according to Table II-1 the total annual usage of the listed materials as solvents is over  $2.8 \times 10^6$  kkg.
3. Of the twenty-four solvents listed in Tables I-1 and I-2, nine are listed for meeting only the ignitability characteristic. These nine spent solvents all have a flash point below  $60^\circ\text{C}$  ( $140^\circ\text{F}$ ) and are thus considered hazardous.

\*The Agency is presently aware that these solvents may contain concentrations of additional toxic constituents listed in Appendix VIII of the regulations. For purposes of this listing, however, the Agency is only listing those wastes for the presence of the halogenated and non-halogenated solvents. The Agency expects to study these listings further to determine whether the waste solvent and still bottom listings should be amended.

TABLE I-1

LISTING CODES FOR HALOGENATED ORGANIC SOLVENTS\*  
(in order of usage as solvent)

Solvents	Listing Codes	Flash Point (°F)
Perchloroethylene	T	-
Methylene chloride	T	-
Trichloroethylene	T	-
1,1,1,-Trichloroethane	T	-
Chlorobenzene	T	-
1,1,2-Trichloro-1,2,2- Trifluoroethane	T	-
o-Dichlorobenzene	T	-
Trichlorofluoromethane	T	-

\*All data in this table are based on information contained in Reference (1). Dashes in place of data mean either the values were not available or (in the case of flash points) not applicable.

TABLE I-2

LISTING CODES FOR NON-HALOGENATED ORGANIC SOLVENTS\*  
(in order of usage as solvent)

Solvents	Listing Codes	Flash Point (°F)
Xylenes	I**	84(2)
Methanol	I,**	54
Toluene	I,T**	39
Methyl ethyl ketone	I,T**	22(3)
Acetone	I**	3
Methyl isobutyl ketone	I,**	61
Carbon disulfide	I,T**	-25
Ethyl acetate	I**	45(2)
Ethyl benzene	I**	59
Ethyl ether	I**	-49(2)
n-Butyl alcohol	I**	115
Isobutanol	I,T**	82
Cresols and cresylic acid	T	-
Cyclohexanone	I**	111(3)
Nitrobenzene	T	-
Pyridine	I,T**	68

\* All data in this table are based on information contained in Reference (1) except as noted. Dashes in place of data mean either that the values were not available or (in the case of flash points) not applicable.

\*\*Because the listed waste typically would contain a large percentage of these solvents, the listed wastes would fail the ignitability characteristic for liquids--a flash point less than 60°C (140°F).

The fifteen solvents listed as either toxic or toxic and ignitable pose a further hazard to human health and the environment. If improperly managed, these solvents could migrate from the disposal site into ground and surface waters, persist in the environment for extended periods of time, and cause substantial hazard to environmental receptors.

The two fluorocarbons, 1,1,2-trichloro-1,2,2-trifluoroethane and trichlorofluoromethanes present a different type of hazard. Due to their high volatility, these two organics can rise into the stratosphere and deplete the ozone, leading to adverse health and environmental effects.

4. Damage incidents resulting from the mismanagement of waste solvents have been reported. These damage incidents are of three types:
  - (a) Fire/explosion damage resulting from ignition of the solvents;
  - (b) Contamination of wells in the vicinity of inadequate waste storage or disposal (with resulting illness in at least one instance); and
  - (c) Direct entry of solvent into a waterway, resulting in fish kills.
5. These damage incidents show that mismanagement occurs and that substantial hazard to human health and the environment may result there from.

### III. SOURCES OF THE WASTE AND TYPICAL DISPOSAL PRACTICES

#### A. Overall Description of Industry Usage\*

The primary solvent-using industries and the quantity of solvents they use annually are as follows:(1)

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\*Large amounts of chemicals listed in Table II-1 are used in such non-solvent applications as chemical feedstock so that the total production of specific solvent chemicals for all applications is often many times larger than the amount used specifically as a solvent.

Table II-1

## RANKING AND AMOUNTS OF THE LISTED SOLVENTS(1)

Chemical Name	Amount Used As Solvent (kg/yr)
Xylenes	489,900
Methanol	317,500
Toluene	317,500
Perchloroethylene	255,800
Methylene chloride	213,200
Methyl ethyl ketone	202,300
Trichloroethylene	188,200
1,1,1-Trichloroethane	181,400
Acetone	86,200
Methyl isobutyl ketone	78,000
Chlorobenzene	77,100
Carbon disulfide	77,100
Ethyl acetate	69,900
Ethyl benzene	54,430
Ethyl ether	54,430
n-Butyl alcohol	45,360
1,1,2-Trichloro-1,2,2-tri-fluoroethane	24,040
Isobutanol	18,600
o-Dichlorobenzene	11,800
Cresols & cresylic acid(a)	11,800
Cyclohexanone	9,072
Nitrobenzene	9,072
Trichlorofluoromethane	9,072
Pyridine	907

(a) Consumption amounts for cresol and cresylic acid were combined.

Paint & Allied Products and Industrial Operations	1,153,500 kkg/yr
Surface Cleaning	610,600 kkg/yr
Pesticide Production	266,700 kkg/yr
Laundry and Dry Cleaning Operations	214,550 kkg/yr
Pharmaceuticals Manufacture	34,740 kkg/yr
Solvent Recovery Operations (Contract and in-house)	499,000 kkg/yr (feedstock)

Table III-1 summarizes the use pattern of the 10 most widely used solvents in the industrial categories listed above. These data illustrate the distinct difference between halogenated and non-halogenated solvents in industrial usage; the chlorinated and other halogenated solvents in Table III-1 are used almost exclusively in the surface cleaning, laundry and dry cleaning categories, whereas the non-halogenated solvents are used primarily in the production categories (paint, pesticides and pharmaceuticals). The ten specific solvents included in this table are believed to account for about 80 percent of all organic solvent usage.(1)

The composition of the spent solvent\* is dependent on its application, but the spent solvent contains up to 90 percent of the original solvent\*\*. Depending on the recovery techniques,

\*Spent solvents include those solvents which are no longer useful without further processing either because they have outlasted their shelf life or because they have been contaminated, or so changed chemically or physically that they are no longer useful as solvent.

\*\*United States Environmental Protection Agency. 1976. Assessment of Industrial Hazardous Waste Practices Electroplating and Metal Finishing Industries - Job Shops PB-264-349.

Table 11-1

USE DISTRIBUTION OF THE 10 MOST WIDELY USED ORGANIC SOLVENTS (1)

(All data in units of 10<sup>3</sup> kg/yr)

	Xylene	Methanol	Toluene	Perchloroethylene	Methylene chloride	Methyl ethyl ketone	Trichloroethylene	1,1,1-Trichloroethane	Acetone	Methyl Isobutyl ketone	Total*
Paints & Allied Products	245	300	292	-	-	165	-	-	91	61	1153
Surface Cleaning	-	-	-	48	213	-	161	153	N/A	-	610
Pesticides	245	-	-	-	-	-	-	14	-	8	267
Pharmaceuticals	N/A	1	25	-	N/A	N/A	-	N/A	N/A	8	34
Laundry & Dry Clean.	-	-	-	208	-	-	7	-	-	-	215
<b>TOTAL</b>	490	301	317	256	213	165	168	157	91	77	
listed Use Level in Reference (1)	490	317	317	256	213	202	165	150	95	76	

\*This total is for the 10 primary solvents only and does not include other solvents used in the respective categories.  
 "N/A" indicates that the solvent at issue is probably used, but the amount that is used is not known.

sludges which result from reclamation processes contain from 1 to 50% of the original solvent.\* However, because of the economic considerations of the reclaiming process, the solvent content of the sludge is seldom reduced below 10 percent.\*\*

B. Solvent Usage in Paint & Allied Products and Industrial Operations

The category of Paint & Allied Products and Industrial Operations is taken here to include the following solvent-use industrial operations:

- ° Paint & Allied Products Manufacture
- ° Roll Coatings
- ° Paper Coatings
- ° Dye Manufacture
- ° Ink Manufacture
- ° Adhesive Manufacture
- ° Printing Operations

¶ The Paint and Allied Products and Industrial operations category accounts for about half of all organic solvent utilization by industry. The Paint and Allied Products portion of this category is the largest solvent-use subcategory, with Printing Operations being the second largest use subcategory.

For the Paint & Allied Products Industry, there are about 1200 paint manufacturing companies that operate more

\*United States Environmental Protection Agency. 1979. Organic Solvent Cleaners-Background Information for Proposed Standards. EPA-45/12-78-045a.

\*\*United States Environmental Protection Agency. 1978. Source Assessment: Reclaiming of Waste Solvents. State of the Art. PB-289-934.

than 1500 plants. Solvents are important ingredients in formulations for solvent-thinned paints, lacquers, and factory-applied coatings.

Solvent containing wastes arise from the use of solvents to clean equipment, and still bottoms from the recovery of the solvents used in production\*. It is estimated<sup>(4)</sup> that approximately one-third of the solvents used for equipment cleaning are reclaimed, and that  $7 \times 10^6$  gallons of solvent are disposed of yearly from this source.

The total quantity of solvent-containing wastes from the paint industry is estimated to contain 14,300 kkg/yr of solvents.<sup>(4)</sup> These are primarily non-halogenated solvents such as xylenes, methanol, acetone, toluene, MEK, etc.

The remaining industrial processes included in this overall category (manufacture of inks, adhesives, dyes, and various types of coatings) utilize organic solvents (primarily non-halogenated) in much the same manner as the paint industry; that is, as an important component of formulations and for equipment cleaning.<sup>(1)</sup> Printing operations also use solvents for cleaning operations and as dye or pigment carriers. The types of waste generated from these industries should be generally similar to those from the paint industry and include:

Equipment cleaning wastes;

Still bottoms from solvent recovery.

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\*Additional waste streams from these industrial categories (such as off-specification product and spills of finished product) are expected to be covered by future listings.

Spent solvents used for equipment cleaning, if not reclaimed, are drummed and landfilled<sup>(4)</sup>. Most paint companies contract for waste disposal services. Solvent recovery still bottoms are incinerated, landfilled, or injected into deep wells.<sup>(5)</sup>

C. Surface Cleaning

The Surface Cleaning category consists of two important subcategories:

- ° Industrial Degreasing
- ° Repair work
  - Industrial Maintenance and Repair
  - Commercial Service and Repair
  - Consumer-performed Maintenance and Repair

About half of the solvents used in Surface Cleaning Operations, as shown in Table III-1, are used in Industrial Degreasing, (see the Listing Background Document for Solvent Degreasing Operations) with the other half being used in various types of repair work.<sup>(1)</sup> According to Reference (6), the total number of degreasing operations in the United States for 1976 was over 1,300,000, of which nearly half were associated with manufacturing operations of various types. The major solvents used are trichloroethylene, 1,1,1-trichloroethane, and chlorofluorocarbons. Most of the solvents used in surface cleaning were halogenated, due to their nonflammable character; this property is especially important in high-temperature degreasing operations.

Neither surface cleaning nor either of its two subcategories can be classified as industry specific, per se; rather, these operations are conducted in a number of types of industries (i.e., primary metals, auto repair shops, textile plants).

With respect to the geographic distribution, industrial degreasing is the most concentrated source of solvent wastes from the surface cleaning category since degreasing is associated with manufacturing operations that involve metal finishing (including etching, plating, priming and painting) and electronic components manufacture. The repair work subcategory is much more diffuse in distribution, with both commercial service and repair and consumer-performed maintenance and repair being generally distributed in the same pattern as the population itself.(5)

The major types of wastes from solvent usage in the industrial degreasing subcategory are used (spent) solvent and solvent recovery still bottoms. Wastes from the repair work subcategory would include both halogenated and non-halogenated solvents, and would take the form of relatively small amounts of used solvent (typically up to a few gallons), plus contaminated rags and other materials.

D. Production of Pesticides, Pharmaceuticals and Other Organic Chemicals

Solvent applications in the production of pesticides, pharmaceuticals and other organic chemicals include usage as

a reaction (synthesis) medium, and usage in equipment cleaning.(1)  
The solvents used are primarily non-halogenated and are typically selected for compatibility with the production process. Toluene is the most widely used solvent in pharmaceuticals manufacture, methanol is used as the reaction solvent in Nylon 66 production, and acetone is used as the solvent in the production of cellulose acetate.(1)

Wastes from solvent usage in these industries take the form of off-specification product material, equipment cleaning wastes, and solvent recovery still bottoms. The destination of all solid wastes is not known, but a large percentage is reclaimed either in-house or by contract recovery operations.(5)

Solvent-containing wastes in these industries are not as geographically distributed as in the other categories discussed herein, but would be expected to follow the general geographical pattern of the organic chemical industry.

#### E. Laundry and Dry Cleaning

There are about 25,000 retail dry cleaning plants in the United States, 18,000 of which use between 167,000 kkg/yr(7) and 208,000 kkg/yr(1) of perchloroethylene. Of the other 7000 plants, 6000 use about 72,700 kkg/yr of Stoddard's solvent\*, (which is a petroleum distillate), and 1000 use trichlorofluoroethane at a rate of about 900 kkg/yr.(7) The

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\*Stoddard solvent is not specifically included in the waste listings, however, since this solvent has a flash point of 105°F (i.e., meets the ignitability characteristic), it would also be regulated under the Subtitle C regulatory control system.

solvents are used to remove dirt, grease and other materials. It is believed that 8 percent<sup>(7)</sup> of the amount of perchloroethylene used in dry cleaning is disposed of along with still-bottom and cooker residues, so that the amount of perchloroethylene discarded is between 13.4 and 16.6 thousand kkg/yr.

The distribution of dry cleaning plants is uniform with respect to population and is especially associated with population in large urban areas.<sup>(7)</sup>

Still bottoms from retail dry cleaning consist of about 60 percent solvent and 40 percent oily residue.<sup>(7)</sup> "Cooker"\* residues are 25 percent solvent and 75 percent spent filter (mostly diatomaceous earth).<sup>(7)</sup>

#### F. Solvent Recovery Operations

Still bottoms from solvent recovery operations are the remaining waste streams included in this listing. Each of the solvent use industry categories discussed above generates feedstocks for solvent recovery operations. Recovery may be accomplished either in-house or by contract to a recovery firm.

With regard to contract solvent recovery operations, there are between 80 and 100 contract solvent recovery operations in the U.S.<sup>(4)</sup> The surface cleaning category, and particularly industrial degreasing operations is one of the largest sources of spent solvents sent to contract reclaimers.

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\*A "cooker" is a type of still in which solvent-contaminated diatomaceous filter powder is heated to drive off the solvent fraction of the total liquid residue contained in the filter powder.

Other important sources of spent solvents are the paint, ink, and coatings manufacturers and manufacturing processes where very pure solvents are used in organic synthesis (e.g., the organic chemical and pharmaceuticals industries).<sup>(8)</sup> Some contract reclaiming of solvents is also carried out on solvents from commercial and industrial dry cleaning operations. The geographic distribution, by state, of contract solvent recovery operations is presented in Table III-2.

The volume of feedstock sent to the contract solvent recovery industry is approximately 287,000 kkg/yr; of this volume, about 27 percent are halogenated.<sup>(4)</sup>

Although there are approximately 100 contract solvent recovery companies, the total number of solvent recovery operations is much larger due to on-site recovery. Of the total number of plants involved in "cleaning operations", 97.89 percent perform on-premises solvent recovery.<sup>(8)</sup>

Excluding the dry cleaning plants, which are distributed geographically in the same pattern as population, the geographic distribution of all solvent recovery operations is as shown in Table III-3.

Solvent recovery still bottoms (sludges) from contract reclaiming operations amount to about 73,900 kkg/yr, of which between 5 and 50 percent is solvent, or an average solvent content of about 25 percent.<sup>(4)</sup> About 27 percent of the solvents in still-bottom sludges are halogenated.<sup>(4)</sup> Thus, the total still bottom waste from contract reclaiming consists of the following components:

Table III-2

GEOGRAPHIC DISTRIBUTION OF CONTRACT SOLVENT  
RECOVERY OPERATIONS(4)

New Jersey	9
California	9
Ohio	8
Illinois	8
Michigan	7
New York	5
Indiana	4
Massachusetts	3
Rhode Island	2
Maryland	2
South Carolina	2
Georgia	2
Kentucky	2
Tennessee	2
Missouri	2
Texas	2
Connecticut	1
North Carolina	1
Florida	1
Kansas	1
Arizona	$\frac{1}{74}$

Table III-3

## STATE DISTRIBUTION OF SOLVENT RECLAIMING OPERATIONS (3)

State	Number of Plants	Percent of Total
Alabama	72	1.8
Arizona	37	0.94
Arkansas	39	0.99
California	424	10.
Colorado	44	0.16
Connecticut	60	1.5
Delaware	12	0.35
Florida	141	3.5
Georgia	98	2.4
Idaho	14	0.4
Illinois	224	5.5
Indiana	113	2.8
Iowa	59	1.4
Kansas	49	1.2
Kentucky	70	1.7
Louisiana	63	2.0
Maine	19	0.5
Maryland	63	2.0
Massachusetts	65	2.0
Michigan	178	4.3
Minnesota	76	1.8
Mississippi	45	1.1
Missouri	93	2.3
Montana	15	0.41
Nebraska	30	0.77
Nevada	10	0.29
New Hampshire	13	0.38
New Jersey	153	3.7
New Mexico	21	0.57
New York	372	8.9
North Carolina	105	2.5
North Dakota	13	0.37
Ohio	213	5.1
Oklahoma	56	1.3
Oregon	40	1.1
Pennsylvania	245	5.9
Rhode Island	21	0.57
South Carolina	55	1.3
Tennessee	63	2.0

Table III-3 (cont'd)

<u>State</u>	<u>Number of Plants</u>	<u>Percent of Total</u>
Texas	242	5.8
Utah	21	0.56
Vermont	8	0.24
Virginia	97	2.3
Washington	72	1.7
West Virginia	41	0.99
Wisconsin	90	2.2
Wyoming	<u>6</u>	<u>0.14</u>
Total	4,158	100

18,250 kkg/yr solvent, including 13,320 kkg/yr non-halogenated and 4,930 kkg/yr halogenated;  
54,750 kkg/yr non-solvent contaminant, including oils, waxes, metals and chlorinated and nonchlorinated organics.

The estimate of 25 percent average solvent content, as presented above, can probably be applied to solvent recovery still bottoms for all of the industries discussed herein, since the technology used to reclaim solvents is roughly similar throughout U.S. industry.(8)

#### Waste Management Practices\*

The most widely used management practices for spent solvents is either recovery/reclamation (either on-site or by contract recovery operations), land disposal (which may include anything from open ground dumping to landfilling), or incineration. For still bottoms, about 80(8) to 86(4) percent of these bottoms from contract solvent reclaimers

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\*The Agency has concluded that it does have jurisdiction under Subtitle C of RCRA to regulate waste materials that are used, reused, recycled or reclaimed. Furthermore, it has reasoned that such materials do not become less hazardous to human health or the environment because they are intended to be used, reused, recycled or reclaimed in lieu of being discarded. Therefore, at this time, applicable requirements of Parts 262 through 265 and 122 will apply to the accumulation, storage and transportation of hazardous wastes that are used, reused, recycled or reclaimed. The Agency believes this regulatory coverage is appropriate to the subject wastes. These spent solvents and still bottoms from the recovery of these solvents are hazardous in so far as they are being accumulated or stored in drums or tanks prior to recycling. Therefore, these wastes will be considered as hazardous whether recycled or disposed. However, at the present time, the management of these wastes during recycling operations will not be regulated.

are incinerated. Still bottom sludges from both contract reclaimers and from solvent recovery operations performed by solvent-using industries, if not incinerated, are either landfilled or injected into deep wells.(8,5) Land disposal of still bottom sludges from contract reclaimers is mostly in landfills that are covered daily.(4) A small amount of sludge is used as asphalt extender (about 0.1 percent).(4)

IV. References to Section III

1. Lee, B.B., G.E. Wilkins and E.M. Nichols. Organic solvent use study. Final Report. EPA No. 560/12-790-002. NTIS PB No. 301 342. 1979.
2. Wildholz, M. (ed.). The Merck Index. 9th ed. Merck and Company. Rahway, New Jersey. 1976.
3. Sax, N. I. Dangerous Properties of Industrial Materials. Van Nostrand Reinhold Publishing Company, New York. 1963.
4. Scofield, F., J. Levin, G. Beeland and T. Laird. Assessment of industrial hazardous waste practices, paint & allied products industry, contract solvent reclaiming operations, and factory application of coatings. EPA No. 530/SW-119c. NTIS PB No. 251 669. September, 1975.
5. Levin, J., G. Beeland, J. Greenberg, and G. Peters. Assessment of industrial hazardous waste practices: Special machinery manufacturing industries. NTIS PB No. 262 981. March, 1977.
6. Goodwin, D. R., and D. G. Hawkins. Organic solvent cleaners - Background information for proposed standards. EPA No. 450/2-78-045a. NTIS PB No. 137 912. October, 1979.
7. International Fabricare Institute. Silver Spring, Maryland. Personal communication with B. Fisher. December, 1979.
8. Tierney, D.R., and T.W. Hughes. Source assessment reclaiming of waste solvents. State of the Art. EPA No. 600/2-78-004f. NTIS PB No. 282 934. April, 1978.

#### IV. HAZARDS POSED BY THE WASTES

##### A. Hazardous Properties of the Solvents

The major halogenated solvents exhibit organic toxic properties which make them potentially hazardous to human health and the environment. In particular, the two halogenated solvents, perchloroethylene and trichloroethylene are on CAG's List of Carcinogens and 1,1,1-trichloroethane is a suspect carcinogen. All of the listed halogenated organic solvents, except 1,1,2-trichloro-1,2,2-trifluoroethane, are priority pollutants under Section 307(a) of the CWA.

A number of the non-halogenated organic solvents also exhibit toxicity properties. For example, nitrobenzene has been identified as a suspect carcinogen. These compounds are toxic via one or more of the exposure routes inhalation, ingestion and/or through the skin. Short term human exposure to these compounds can have numerous adverse effects. (For more information on the adverse health effects of these halogenated and non-halogenated solvents, see Health and Environmental Effects, pp. 38-45. In addition, almost all of the non-halogenated solvents also present an ignitability hazard.

In light of the health hazards associated with the waste

solvents--particularly those which are genetically active-- and the high concentrations of hazardous solvents contained in the waste, the Agency believes a decision not to list these waste solvents as hazardous would be warranted only if the Administrator were convinced that waste solvents could not migrate and persist, reaching human or environmental receptors (if improperly managed). Such assurance does not appear possible. Not only do all of the waste solvents in varying degrees, have significant potential for migration, mobility, and persistence, but many have been implicated in actual damage incidents as well. The Administrator thus believes the hazardous waste listing to be warranted.

In addition, almost all non-halogenated solvents also present an ignitability hazard. According to Table I-2, the fourteen most-used non-halogenated organic solvents exhibit flash points of 115°F or below, and are thus well below the limit set for defining an ignitable waste under RCRA §261.21 (flash point below 140°F); therefore, these spent solvents and the still bottoms from the recovery of these solvents are defined as hazardous.

Based on the information in Section III, most of the wastes from usage of organic solvents are landfilled or incinerated. Smaller amounts of these solvent wastes are either placed on open land (or dumps), into storm sewers, and into deep wells. Mismanagement and improper disposal of these

wastes by any of these methods could result in a substantial health and environmental hazard.

Actual damage incidents (see pp. 32-35) involving certain of these listed wastes confirm the dangers of ignitability, and of leaching of waste constituents from landfills to groundwater. Improper waste incineration could also lead to substantial hazard. Thus, inadequate incineration conditions (temperature and residence time) can result in emission of solvents or toxic degradation products. Where a chlorinated solvent is involved, emissions could be more dangerous than the waste itself. For example, phosgene is a partially combusted chlorinated organic (halogenated solvent) which is produced by the decomposition or combustion of chlorinated organics by heat.(1a,1b,1c) Phosgene has been used as a chemical warfare agent and is recognized as extremely toxic.

B. Migratory Potential and Persistence of Halogenated And Non-Halogenated Solvents

The following section discusses the migratory potential, mobility, and persistence of the individual waste solvents. In general, all of these solvents appear capable of sufficient migration, mobility and persistence to create a substantial hazard should waste mismanagement occur.

Environmental fate data showing the potential for release of the individual halogenated and non-halogenated solvents is

described below and summarized in Table IV-1 and Table IV-2.

Perchloroethylene

Perchloroethylene, if not properly disposed of, may migrate from the waste into the environment via both air and groundwater exposure pathways.

Having been detected in several sites away from the disposal area (i.e., found in varying amounts in school basement air, in basement sumps, and on solid surface samples at the Love Canal site), perchloroethylene has indeed been demonstrated to be quite mobile and persistent.<sup>9</sup>

Methylene Chloride

Methylene chloride, if not properly managed, may migrate from the waste into the environment. It is very water-soluble (20,000 mg/l), thus could leach into groundwater and persist there due to its stability.<sup>10</sup> It is also very volatile (350 mm Hg at 20°C) and could present an air pollution problem because of its high evaporation rate (1.8 times the rate of ether) and its stability in air and light.<sup>10</sup>

Trichloroethylene

Trichloroethylene, if not properly managed, may migrate from the disposal site into the environment via air and groundwater pathways. First, it is volatile (77 mm Hg at 20°C, 141.04 mm Hg at 40°C<sup>8</sup>), so it may be released from the waste into the air; it has been detected in school and basement air at the Love Canal site.<sup>9</sup>

TABLE IV-1

Halogenated Solvents\*

Compound	Vapor Pressure (mm Hg)	Solubility in Water (mg/l)	Octanol/Water Partition Coefficient
Perchloroethylene	19 at 25°C <sup>5</sup>	150 at 25°C <sup>5</sup>	339 <sup>2</sup>
Methylene chloride	350 at 20°C	20,000 at 25°C <sup>5</sup>	20
Trichloroethylene	77 at 25°C <sup>5</sup>	1,000 at 20°C <sup>5</sup>	195 <sup>2</sup>
1,1,1-Trichloroethane	100 at 20°C	950 at 25°C	158
Chlorobenzene	10 at 22°C	488 at 25°C	690
1,1,2-Trichloro- 1,2,2-Trifluoroethane	270 at 20°C	10 at 25°C	100
1,2-Dichlorobenzene	1.56 at 25°C <sup>5</sup>	145 at 25°C	2400 <sup>2</sup>
Trichlorofluoromethane	687 at 20°C <sup>11</sup>	1,100 at 25°C <sup>11</sup>	339 <sup>2</sup>

\* Table compiled from data given in "Physical Chemical Properties of Hazardous Waste Constituents" (U.S. EPA, 1980) unless otherwise specified by superscript.

Table IV-2

Non-Halogenated Solvents\*

Compound	Vapor Pressure (mm Hg)	Solubility in Water	Octanol/Water Partition Coefficient
Methanol	100 at 21.2°C	Miscible	5
Toluene	28.4 at 25°C	470 at 25°C	117
Methyl ethyl ketone	100 at 25°C	100,000 at 25°C	1
Methyl isobutyl ketone	16 at 20°C	19,000 at 25°C	1
Carbon disulfide	260 at 20°C	2,200 at 25°C	100
Isobutanol	10 at 25°C	95,000 at 18°C	8
Cresols and cresylic acid ortho (1,2)	0.24 at 25°C <sup>11</sup>	31,000 at 40°C <sup>11</sup>	110 <sup>2</sup>
meta (1,3)	0.04 at 20°C <sup>11</sup>	23,500 at 20°C <sup>11</sup>	102 <sup>2</sup>
para (1,4)	0.11 at 25°C <sup>11</sup>	24,000 at 40°C <sup>11</sup>	98 <sup>2</sup>
Nitrobenzene	1 at 44.4°C	1,900 at 25°C	62
Pyridine	20 at 25°C	Miscible	5

\*Table compiled from data given in "Physical Chemical Properties of Hazardous Waste Constituents" (U.S. EPA, 1980) unless otherwise specified by superscript.

It is also relatively water-soluble (1,000 mg/l), so that it may leach into groundwaters if not adequately contained. Trichloroethylene has been detected in a number of wells and residue ponds near groundwater contaminated by a chemical company dump, as well as in basement sumps at the Love Canal site, confirming its mobility and persistence in groundwater.<sup>9</sup>

#### 1,1,1-Trichloroethane

1,1,1-Trichloroethane is a highly mobile compound, and if not properly managed, could migrate from wastes into the environment. It is highly volatile (100 mm Hg at 20°C; approximately 210 mm Hg at 40°C), so that it may be released from waste sites into the air. Once in the air, it will only decompose at elevated temperatures. Because of this, and the fact that 1,1,1-trichloroethane is reactive to sunlight at high altitudes, while stable at low altitudes, it may create air-pollution problems if disposed of inadequately.<sup>10</sup> It has been detected in school and basement air at the Love Canal site.<sup>9</sup>

1,1,1-trichloroethane is also relatively water-soluble (950 mg/l) and mobile, particularly where soils are low in inorganic content.<sup>10</sup> It is also relatively persistent in groundwater where it reacts slowly, releasing hydrochloric acid.<sup>10</sup>

#### Chlorobenzene

Chlorobenzene may migrate from the disposal site into the environment if inadequately disposed of. Its water solubility is fairly high (488 mg/l) to enable its leaching into groundwater where it would persist, since it is not amenable to hydrolysis.<sup>10</sup>

Chlorobenzene is also volatile so it could be released from wastes into the air.<sup>10</sup> It has been detected in school and basement air, basement sumps, and solid surface samples at the Love Canal site.<sup>9</sup> Because it does not biodegrade well, chlorobenzene is very persistent in the environment.<sup>10</sup>

1,1,2-Trichloro-1,2,2-trifluoroethane/Trichlorofluoromethane

These two solvents, if improperly managed, can migrate from the disposal site into the environment. They are extremely volatile (1,1,2-trichloro-1,2,2-trifluoroethane-270 mm Hg at 20°C, to over 500 mm Hg at 40°C;<sup>10</sup> trichlorofluoromethane-687 mm Hg at 20°C<sup>7</sup>) and very persistent in the environment due to resistance to biodegradation, photodecomposition, and chemical degradation.<sup>7</sup> Because of their high volatility and persistence, after release at the surface of the earth, these solvents rise to the stratosphere where they may release chlorine atoms and deplete the ozone. This can lead to various adverse health and environmental effects resulting from an increase in the amount of ultraviolet radiation reaching the earth, as well as possible changes in the earth's climate induced by the "greenhouse effect".<sup>3,4</sup>

o - Dichlorobenzene

o - Dichlorobenzene, if disposed of improperly, may migrate from the disposal site into the environment by both air and water pathways. Having been detected at several sites away from the disposal area (found in school and basement air, in basement sumps, and in solid surface samples at

the Love Canal site), o-dichlorobenzene has been demonstrated to be mobile and persistent.<sup>9</sup>

o-Dichlorobenzenes has a very high octanol/water partition coefficient of 2,400, indicating a high bioaccumulation potential. Thus, migration, even in small concentrations, could lead to a chronic toxicity hazard (Appendix A).

#### Toluene

Toluene, if improperly managed, may migrate from the the disposal site into the environment. It is relatively volatile (vapor pressure 28 mm Hg at 20°C) and so can migrate via and air pathway. It can re-enter the hydrosphere in rain.<sup>12</sup> Toluene is also capable of migration via a groundwater pathway since it is relatively soluble (470 mg/l), and persistent in abiotic environments (such as most aquifers).

Toluene has been detected in school and basement air, basement sumps, and solid surface samples at the Love Canal site, demonstrating its mobility and persistence in both air and groundwater.<sup>9</sup>

#### Methyl Ethyl Ketone

Methyl ethyl ketone, if disposed of inadequately may migrate from the disposal site into the environment. It is extremely soluble in water (100,000 mg/l), and therefore could leach into groundwater. It is also very volatile (185.4 mm Hg at 40°C<sup>8</sup>), and could present an air pollution problem if improperly contained. Because of its high solubility

it could be re-entrained from air into the hydrosphere via rain.

Methyl ethyl ketone has been detected at several sites near groundwater contaminated by an old chemical company dump, as well as in school and basement air at the Love Canal site, demonstrating both its mobility and persistence.<sup>9</sup>

#### Carbon Disulfide

Carbon disulfide, if improperly managed, may migrate from the disposal site into the environment. It is extremely volatile (260 mm Hg at 20°C) and although subject to photolysis, could present an air pollution problem if inadequately contained. It is also quite soluble in water (2200 mg/l), and is not known to attenuate in soils; therefore it could leach into the groundwater, where, being unamenable to hydrolysis, it is likely to persist for an extended time period.<sup>10</sup>

#### Isobutanol

Isobutanol, if improperly managed, may migrate from the disposal site into the environment. It is extremely water-soluble (95,000 mg/l); thus, if inadequately contained, it may contaminate surface water and adversely affect its self-purification ability.<sup>10</sup> In addition, isobutanol could leach into groundwater if disposal is inadequate.

#### Cresols (and cresylic acid)

Cresols, if improperly managed, may migrate from the disposal site into the environment. Cresols are highly soluble (23,500 to 31,000 mg/l) and are not known to attenuate

significantly in soils; thus, they could leach into groundwater if disposal is inadequate. Once in water, cresols rapidly form chlorinated compounds, which are more environmentally objectionable.<sup>10</sup> Cresols are not known to hydrolyze and so would be likely to persist in groundwater.<sup>10</sup>

#### Nitrobenzene

Nitrobenzene, if disposed of inadequately, may migrate from the disposal site into the environment. It is water-soluble (1900 mg/l) and would be mobile where soil organic content is low,<sup>10</sup> and thus could leach into groundwater if disposal is not adequate. It is likely to be highly persistent in groundwater since it is not amenable to hydrolysis and does not biodegrade well.<sup>10</sup>

#### Pyridine

Pyridine, if disposed of inadequately, may migrate from the disposal site. Because pyridine is miscible with water, it has high migratory potential. It would be mobile as well, unless soil has high clay content.<sup>10</sup> Pyridine also would be likely to persist in the abiotic environment of most groundwaters.

#### C. Mismanagement of Wastes Destined for Land Disposal

Documented damage incidents resulting from the mismanagement of these wastes from usage of organic solvents are presented below:

### Damage Resulting from Ignitability of Wastes

- (1) A load of used pesticide containers delivered to a disposal site in Fresno County, California, also contained several drums of an acetone-methanol solvent mixture. When the load was compacted by a bulldozer, the waste ignited, engulfing the bulldozer in flames and dispersed pesticide wastes.(13)
- (2) A large number of drums containing organic solvent wastes were deposited in a landfill at Contra Costa, California. In the immediate area were leaking containers of concentrated mineral acids and several bags of beryllium wastes in dust form. The operators failed to cover the wastes at the end of the day. The combination of wastes ignited during the night, starting a large chemical fire which possibly dispersed toxic beryllium oxide.(13)
- (3) Two serious fires at the Merl-Milam Landfill, St. Clare County, Illinois (August, 1973 and April, 1974) were attributed to the presence of solvent wastes from plastics manufacture.(13)

### Contamination of Groundwaters

- (1) In two separate instances in Michigan, trichloroethylene was dumped on the ground and later found to have migrated into groundwater. In one case, trichloroethylene dumped at a rate of 1000 gallons per year over a four-year period was detected in residential wells as much as 1100 feet from the site of dumping. Concentrations ranged as high as 28 ppm.(13)

In the other case, the Air Force at a base near Oscoda, Michigan, had problems with contaminated groundwater because of a leaking tank which use to hold trichloroethylene. The problem was compounded when a waste hauler apparently mismanaged the trichloroethylene that was hauled from the leaking tank, and groundwater contamination up to four miles away was considered one of the results.(11)

- (2) A sump overflow in 1971 at the Superior Tube Company allowed trichloroethylene wastes to leak into a cooling pond. Seepage from this pond was found to contaminate a private well 75 yards distant and a company well at the site.(13)
- (3) Open dumping of wastes, including solvent wastes, from a chemical packing plant by U.S. Aviox Company resulted in entry of organic solvents into the water table and contamination of several nearby water wells in 1973. One family reported illness resulting from use of the contaminated well water.(13)
- (4) [Mono]chlorobenzenes, at concentrations of 5 mg/l and 30 mg/l has been detected in the water from 2 of 21 observation wells, installed at depths up to 50 feet at varying distances from an industrial manufacturing complex devoted to the development and manufacture of engineering plastics.(14)

The damage incidents presented above illustrate the following potential hazards associated with wastes from usage of organic solvents:

- (1) Ignitability hazard during mismanagement;
- (2) Potential toxicity hazard to humans via groundwater exposure pathways.

IV. References to Section IV (A, B and C)

1. Jacobs, S. The handbook of solvents. D. Van Nostrand Company, Inc. New York. 1957.
- 1a. Edwards, J.B. Combustion formulation and emission of trace species. Ann Arbor Science. 1977.
- 1b. NIOSH. Criteria for a recommended standard: Occupational exposure to phosgene. HEW, PHS, CDC, NIOSH. NTIS PB No. 267 514. 1976.
- 1c. Chemical and Process Technology Encyclopedia. McGraw Hill. 1974.
2. Leo, A., C. Hansch and D. Elkins. Partition coefficients and their uses. Chem. Rev. 71:525-616. 1971 (Updated 1977).
3. National Academy of Sciences, National Research Council. Halocarbons: Environmental effects of chloromethane release. Publication No. 2529. 1976.
4. National Academy of Sciences, National Research Council. Committee on Impacts of Stratospheric Change. Stratospheric ozone depletion by halocarbons: Chemistry and transport. 1979.
5. Patty, F.A., ed. Industrial hygiene and toxicology. Interscience Publishers, New York. 1963.
6. Sax, N. I. Dangerous properties of industrial materials, 5th ed. Van Nostrand Reinhold Company, New York. 1979.
7. U.S. EPA. Environmental hazard assessment of one- and two-carbon fluorocarbons. EPA No. 560/2-75-003. NTIS PB No. 246 419. 1975.
8. U.S. EPA. Evaluation of treatment, storage, and disposal techniques for ignitable, volatile, and reactive wastes. Contract Number 68-01-5160. (Draft final report). 1980.
9. "Love Canal Public Health Bomb", A Special Report to the Governor and Legislature, New York State Department of Health. 1978.
10. U.S. EPA. Physical chemical properties of hazardous waste constituents. (Prepared by Southeast Environmental Research Laboratory; Jim Falco, Project Officer). 1980.
11. Verschueren, K. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Company, New York. 1977.

12. Walker, P. Air pollution assessment of toluene.  
NTIS PB No. 256 735. May, 1976.
13. U.S. EPA. Open Files. Hazardous Site Control Branch,  
WH-548, U.S. EPA. 401 M St., S.W., Washington, D.C. 20460.  
Contact Hugh Kauffman. (202) 245-3051.
14. TSCA Section 8(e) notice from General Electric Company to  
U.S. EPA, Region I Permits Branch, January 23, 1980.

D. Health and Environmental Effects\*

Perchloroethylene (Tetrachloroethylene)

Perchloroethylene (PCE) was reported carcinogenic to mice.<sup>(16)</sup> It has also been identified by the Agency as a chemical which has demonstrated substantial evidence of being carcinogenic. PCE is chronically toxic to rats and mice, causing kidney and liver damage;<sup>(10,16,21)</sup> and to humans, causing impaired liver function.<sup>(2)</sup> Subjective central nervous system complaints were noted in workers occupationally exposed to PCE.<sup>(14)</sup> PCE exposure is reported to cause alcohol intolerance to humans.

PCE is a priority pollutant under Section 307(a) of the Clean Water Act.

Methylene Chloride (Dichloromethane)

EPA has found "suggestive" evidence of the carcinogenicity of methylene chloride, therefore, methylene chloride is considered a "suspect carcinogen" (Appendix A); methylene chloride was also reported as being mutagenic to a bacterial strain, S. typhimurium.<sup>(24)</sup> It was reported to be fetotoxic or embryo-toxic to rats and mice.<sup>(23)</sup> Female workers had gynecological problems after prolonged exposure to methylene chloride.<sup>(36)</sup> Methylene chloride also causes central nervous system depression and elevation of carboxyhemoglobin levels.<sup>(18)</sup> Severe contamination of food or water can cause irreversible renal and hepatic injury.<sup>(30)</sup> Acute toxicity values range from 147,000 to 310,000 ug/l for aquatic

\*Ethyl benzene, which is only being listed for its ignitability hazard, is also considered a priority pollutant under Section 307(a) of the Clean Water Act.

organisms (Appendix A)

Trichloroethylene

Trichloroethylene (TCE) has been reported to be carcinogenic to mice.(15) It has also been identified by the Agency as a chemical which has demonstrated substantial evidence of being carcinogenic.(38) Industrial exposure to TCE caused some cases of central nervous system disturbances (headaches, insomnia, tremors) as well as peripheral nervous system impairment (neuritis, temporary loss of tactile sense, finger paralysis).(1,13) Rare cases of hepatic damage have been reported following repeated abuse of TCE.(6)

TCE was found to be toxic in varying degrees to several freshwater organisms.(28) There was also a 50% decrease noted in <sup>14</sup>C uptake by a saltwater algae at a concentration of 8,000 mg/l.(20)(Appendix A)

1,1,1-Trichloroethane (Methyl Chloroform)

Data regarding the carcinogenicity of 1,1,1-trichloroethane is inconclusive.(17) It is mutagenic in the Ames test, and in a mammalian cell transformation system (See Appendix A). Chronic exposure, albeit is greater than ambient levels, can cause central nervous system disorders in humans. Animal studies showed toxic effects on the central nervous system, cardiovascular system, pulmonary system, and induced liver and kidney damage.(34) 1,1,1-Trichloroethane is a priority pollutant under Section 307(a) of the Clean Water Act.

### Chlorobenzene (Monochlorobenzene, MCB)

Chlorobenzene has been found to produce histopathological changes in the lungs, liver, and kidneys following its inhalation by rats, rabbits and guinea pigs.<sup>(7)</sup> Oral administration of monochlorobenzene to rats was reported to cause growth retardation in males.<sup>(11)</sup> MCB also appears to increase the activity of some microsomal enzyme systems, which enhances the metabolism of many drugs, pesticides, and other xenobiotics.<sup>(29)</sup>(Appendix A)

MCB was reported to be toxic to varying degrees to several fresh- and salt-water organisms, including algae,<sup>(28)</sup> has a high biomagnification factor (Appendix B), is resistant to biodegradation and hydrolysis and is, therefore, persistent.

MCB is a priority pollutant under Section 307(a) of the Clean Water Act, is a subject of TSCA section 4 Test Rule, and has been selected for bioassay by NCI. These regulatory actions point to concern regarding its toxicity.

### 1,1,2 Trichloro-1,2,2 trifluoroethane

The Agency's primary concern in listing this solvent is the air pollution hazard resulting from its release at the surface of the earth. This can have many adverse health and environmental effects including increased incidence of skin cancer, reduced productivity in several important agricultural crops, and increased mortality in the larvae forms of several important seafood species resulting from the depletion of the ozone.<sup>(39,40)</sup> Because of these effects, EPA is currently considering regulation of CFC production and use.

### 1,2-Dichlorobenzene (ortho isomer)

Ortho 1,2-dichlorobenzene exhibits moderate toxicity via inhalation and oral routes. The major toxicological effect is injury to the liver and kidneys; it is also a central nervous system depressant after short periods of exposure (19,22) (Appendix A).

1,2-dichlorobenzene is designated a priority pollutant under section 307(a) of the Clean Water Act.

### Trichlorofluoromethane

The Agency's primary concern in listing this solvent is the air pollution hazard resulting from its release at the surface of the earth. This can have many adverse health and environmental effects including skin cancer resulting from the depletion of the ozone (Vide Sufora). (39,40) However, additional adverse health effects have been found and are presented below.

Exposure of rabbits to trichlorofluoromethane was reported to cause cardiac arrhythmias. (26) It induced cardiac arrhythmias, sensitized the heart to epinephrine-induced arrhythmias, and caused tachycardia (increased heart rate) myocardial depression, and hypertension in the monkey, dog, rat and mouse. (26)

Trichlorofluoromethane is a priority pollutant under Section 307(a) of the Clean Water Act.\*

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\*The Agency has recently proposed to remove trichlorofluoromethane from the list of toxic pollutants under §307(a) of the Clean Water Act (45 FR 46103, July 9, 1980).

## Toluene

Toluene is a toxic chemical absorbed into the body by inhalation, ingestion, and through the skin. Data on its mutagenicity and carcinogenicity are inconclusive, but it has been reported to cause chromosomal change; teratogenic problems were also recently reported.(47) The acute toxic effect is central nervous system depression, (45) and irritation of eye and throat. These effects occur at low concentrations [200 ppm].(46) Chronic occupational exposure to toluene has led to the development of neuro-muscular disorders. Occupational exposure to female workers to toluene reported to cause several reproductive problems, both to the woman and the offspring.(25) Chronic toluene exposure can cause dermatitis, affect the immune system, and cause permanent damage to the central nervous system.(48)

Since toluene is metabolized in the body by a protective enzyme system which is also involved in the elimination of other toxins, it appears that over-loading the metabolic pathways with toluene may greatly reduce the clearance of other more toxic chemicals. Additionally, the high affinity of toluene for fatty tissue can assist in the absorption of other toxic chemicals into the body. Thus, synergistic effects of toluene on the toxicities of other contaminants may render the waste stream more hazardous (Appendix A).

Toluene is a priority pollutant under Section 307(a) of the Clean Water Act.

### Methyl Ethyl Ketone

Methyl ethyl ketone is a highly volatile ignitable liquid of moderate toxicity via ingestion which can affect the peripheral nervous system and is an experimental teratogen (Appendix A). It is also a strong irritant of the mucous membranes of the eyes and nose. A lethal dose in animals (LC50 - 700 ppm) has caused marked congestion of the internal organs and slight congestion of the brain. Lungs also showed emphysema (Appendix A).

### Carbon Disulfide

Short term human exposure to low atmospheric concentrations of carbon disulfide may result in central nervous system depression, headaches, breathing difficulty and gastrointestinal disturbances. Exposure to short term but high atmospheric concentrations can lead to narcosis and death. The symptoms of humans subjected to repeated exposure to high concentrations or prolonged exposure to low concentrations include insomnia, fatigue, loss of memory, headache, melancholia, vertigo and loss of appetite. Visual impairment, loss of reflexes, and lung irritation has been reported.(19,22) Rats and mice exposed 8 hours per day for 20 weeks to an average concentration of 37 ppm carbon disulfide showed evidence of toxic effects.(19)(Appendix A)

### Isobutanol

Rats receiving isobutyl alcohol, either orally or subcutaneously, one to two times a week for 495 to 643 days showed liver carcinomas and sarcomas, spleen sarcomas and myeloid leukemia.(43)

Ingestion of one molar solution of isobutyl alcohol in water by rats for 4 months did not produce any inflammatory reaction of the liver. However, rats ingesting a two molar solution for two months developed Mallory's alcoholic hyaline bodies in the liver and were observed to have decreases in fat, glycogen, and RNA in the liver.(43)

Acute exposure to isobutyl alcohol causes narcotic effects, and irritation to the eyes and throat in humans exposed to 100 ppm for repeated 8 hour periods. Formation of facuoles in the superficial layers of the cornea and loss of appetite and weight were reported among workers subjected to an undetermined but apparently high concentration, of isobutyl alcohol.(44)  
(Appendix A)

### Pyridine

Pyridine exhibits moderate toxicity when absorbed into the human body through oral, dermal, and inhalation routes.(22) Liver and kidney damage has been produced in animals and man after oral administration.(3) In small doses, conjunctivitis, dizziness, vomiting, diarrhea and jaundice may appear; tremors and ataxia, irritation of the respiratory tract with asthmatic breathing, paralysis of eye muscles, vocal cords and bladder also have been reported.(22)

Adverse taste in fish (carp, rudd) has been reported at 5 ppm. Pyridine causes inhibition of cell multiplication in algae and bacteria at 28 and 340 ppm respectively.(35)(Appendix A)

### Nitrobenzene

Nitrobenzene is a suspected carcinogen.<sup>(4)</sup> When administered to pregnant rats, it caused abnormalities in some of the fetuses examined.<sup>(8)</sup> Changes were observed in the chorionic and placental tissues of pregnant workers exposed to nitrobenzene,<sup>(4)</sup> and menstrual disturbances after chronic exposure have been reported. Chronic exposure to nitrobenzene has been found to cause a variety of blood-variety disorders.

Nitrobenzene is toxic in varying degrees to several salt- and fresh-water organisms.<sup>(31)</sup> (Appendix A), and nitrobenzene is a priority pollutant under Section 307(a) of the Clean Water Act.

### Cresols (Cresylic Acid)

Cresol is highly toxic if orally administered, and moderately toxic if inhaled. Absorption may result in damage to kidney and liver as well as the central nervous system.<sup>(22)</sup> Exposure to cresol can cause severe skin burns and dermatitis.<sup>(19,22)</sup> (Appendix A)

VII. References to Section IV, D

1. Bardodej, A., and J. Vyskocil. The problem of trichloroethylene in occupational medicine. AMA Arch. Ind. Health. 13:581. 1956.
2. Coler, H.R., and H. R. Rossmiller. Tetrachloroethylene exposure in a small industry. Ind. Hyg. Occup. Med. 8:227. 1953.
3. Deichmann, W.R. Toxicology of drugs and chemicals. Academic Press Inc., New York. 1969.
4. Dorigan, J. and J. Hushon. Air pollution assessment of nitrobenzene. NTIS PB No. 257 776. May, 1976.
5. Gosselin, R.E., et. al. Clinical toxicology of commercial products, 4th ed. The Williams and Wilkin Company, Baltimore. 1976.
6. Huff, J.E. New evidence on the old problems of trichloroethylene. Ind. Med. 40:25. 1971.
7. Irish, D.D. Halogenated hydrocarbons:II. Cyclic. In Industrial hygiene and toxicology, V.II, 2nd ed. F. A. Patty, ed. Interscience, New York. p. 1333. 1963.
8. Kazanina, S.S. Morphology and histochemistry of hemochorial placentas of white rats during poisoning of the maternal organisms by nitrobenzene. Bull. Exp. Biol. Med.(USSR) 65:93. 1968.
9. Not used in text.
10. Klaassen, C.D., and G.L. Plaa. Relative effects of chlorinated hydrocarbons on liver and kidney function in dogs. Toxicol. Appl. Pharmacol. 1967.
11. Knapp, W. K., Jr., et al. Subacute oral toxicity of monochlorobenzene in dogs and rats. Toxicol. Appl. Pharmacol. 19:393. 1971.
12. Not used in text.
13. McBirney, B.S. Trichloroethylene and dichloroethylene poisoning. AMA Arch. Ind. Hyg. 10:130. 1954.

14. Medek, V., and J. Kovarik. The effects of perchloroethylene on the health of workers. Pracovni Lekarstvi 25:339. 1973.
15. National Cancer Institute. Carcinogenesis bioassay of trichloroethylene. NCI-CG-TR-2. NTIS PB No. 264 122. 1976.
16. National Cancer Institute. Bioassay of tetrachloroethylene for possible carcinogenicity. NCI-CG-TR-13. NTIS PB No. 272 940. 1977.
17. National Cancer Institute. Bioassay of 1,1,1-trichloroethane for possible carcinogenicity. NCI-CG-TR-3. NTIS PB No. 265 082. 1977.
18. National Institute for Occupational Safety and Health. Criteria for a recommended standard: Occupational exposure to methylene chloride. HEW Pub. No. 76-138. U.S. DHEW. Cincinnati, Ohio. 1976.
19. Patty, F.A., ed. Industrial hygiene and toxicology. Volume II. Interscience Publishers, New York. 1963.
20. Pearson, C.R., and G. McConnell. Chlorinated C<sub>1</sub> and C<sub>2</sub> hydrocarbons in the marine environment. Proc. R. Soc. London B 189:302. 1975.
21. Rowe, V. K., et al. Vapor toxicity of tetrachloroethylene for laboratory animal and human subjects. AMA Arch. Ind. Hyg. Occup. Med. 5:566. 1952.
22. Sax, N. I. Dangerous properties of industrial materials, 5th ed. Van Nostrand Reinhold Company, New York. 1979.
23. Schwetz, B. A., et al. The effects of maternally inhaled trichloroethylene, perchloroethylene, methyl chloroform, and methylene chloride on embryonal and fetal development in mice and rats. Toxicol. Appl. Pharmacol. 32:84. 1975.
24. Simmon, V. F., et al. Mutagenic activity of chemicals identified in drinking water. S. Scott, et al. eds. In: Progress in genetic toxicology. 1977.
25. Syrovadko, O. N. Working conditions and health status of women handling organosiliceous varnishes containing toluene. Gig. Tr. Prof. Zabol. 12:15. 1977.
26. U.S. EPA. Environmental hazard assessment report: Major one- and two-carbon saturated fluorocarbons; review data. EPA No. 560/8-76-003. NTIS PB No. 257 371. August, 1976.
27. Not used in text.

28. U.S. EPA. In-depth studies on health and environmental impacts of selected water pollutants. Contract No. 68-01-4646. 1978.
29. U.S. EPA. Chlorinated benzenes: Ambient water quality criteria. NTIS PB No. 297 919. 1979.
30. U.S. EPA. Halomethanes: Ambient water quality criteria. NTIS PB No. 296 797. 1979.
31. U.S. EPA. Nitrobenzenes: Ambient water quality criteria. NTIS PB No. 296 801. 1979.
32. U.S. EPA. Tetrachloroethylene: Ambient water quality criteria. NTIS PB No. 292 445. 1979.
33. Not used in text.
34. U.S. EPA. Chlorinated ethanes: Ambient water quality criteria. NTIS PB No. 297 920. 1979.
35. Verschueren K. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Company, New York, 1977.
36. Vozovaya, M.A. Gynecological illnesses in workers of major industrial rubber products plants occupations. Gig. Tr. Sostoyanie Spetsificheskikh Funkts. Tab. Neftekhim. Khim. Prom-Sti. (Russ.) 56. (Abstract). 1974.
37. Not used in text.
38. U.S. EPA. Office of Research and Development. Carcinogen Assessment Group. List of Carcinogens. April 22, 1980.
39. National Academy of Sciences, National Research Council. Halocarbons: Environmental effects of chloromethane release. PB No. 2529. 1976.
40. National Academy of Sciences, National Research Council. Committee on Impacts of Stratospheric Change. Stratospheric ozone depletion by halocarbons: Chemistry and transport. 1979.
41. Linari, F., G. Perrelli, and D. Varese. Clinical observations and blood chemistry tests among workers exposed to the effect of a complex ketone--methyl isobutyl ketone. Arch. Sci. Med. 226-237. 1964. (Ital).
42. Specht, H., J.W. Miller, P.J. Valaer, and R.R. Sayers. Acute response of guinea pigs to the inhalation of ketone vapors. NIH Bulletin No. 76. Federal Security Agency. Public Health Service, National Institute of Health. p. 66.

43. Gibel, et al. Exp. Chir. Forsch. 1:235. 1974.
44. Smith et al. Arch. Ind. Hyg. Occup. Med. 10:61. 1954.
45. U.S. EPA. Toluene: Ambient water quality criteria. NTIS PB No. 296 805. 1979.
46. NIOSH. Registry of toxic effects of chemical substances. Toluene. 1978.
47. Nawrot, P. S., and R. E. Stapler. Embryofetal toxicity and teratogenicity of benzene and toluene in the mouse (abstract). Teratology. 19:41a.
48. Cohr, K. H., and J. Stockholm. Toluene—a toxicologic review. Scand. J. Environ. and Health. 5:71-90. 1979.

Response to Comments (Proposed Listings (December 18, 1978))

- ° One commenter objected to the listing "Waste non-halogenated solvent (such as methanol, acetone, isopropyl alcohol, polyvinyl alcohol, stoddard solvent and methyl ethyl ketone) and solvent sludges from cleaning, compounding milling and other processes."\* The commenter argued that without indicating the concentration or quantity of the solvent in the waste, the Agency would be listing wastes as hazardous even if the solvent were present in small concentrations and quantities.

In the listing promulgated today for waste solvents, the Agency is only listing those spent solvents or still bottoms from the recovery of these solvents which would contain substantial quantities and concentrations of the solvent. For example, spent solvents can contain up to 90% of the original solvent while the still bottoms may contain up to 50% of the spent solvent.

- ° A number of commenters objected to the listing of polyvinyl alcohol (PVA) as a solvent. These commenters argued that PVA is not a solvent but is a solid and can only be used as a solute. Therefore, they recommended that PVA be removed from the list.

\*This specific listing will not be included in the final regulation; however, it will be covered under the generic listing "The Spent non-halogenated solvents...."

The Agency agrees with the commenters and therefore, has removed PVA from the listing.

- A number of commenters objected to the listing of waste halogenated/non-halogenated solvents. They felt that the listing was too vague and ambiguous.

In the listings promulgated today, the Agency has specifically listed only those solvents for which data or information are available which indicates a present or potential hazard could be posed to human health and the environment if improperly managed. Therefore, the listing description promulgated today should respond to the commenters' objection.

Response to Comments - Spent Halogenated and Non-Halogenated Solvents and the Still Bottoms/Sludges From the Recovery of These Solvents

A number of comments were received with respect to wastes F001 to F005 (Spent halogenated and non-halogenated solvents and the still bottoms/sludges from the recovery of these solvents).

1. One commenter requested that the Agency clarify or define what it means by the term "spent". For example, the commenter questioned whether "spent" refers to the state of the chemical which was pure initially but now appears in the waste stream after being used, or whether it refers to the altered or decomposed state of a chemical which has outlasted its shelf life.

The Agency agrees with the commenter and has thus included the following definition for "spent solvents" in the listing background documents:

"Spent solvents include those solvents which are no longer useful as solvents without further processing (i.e., solvent reclamation), either because the solvents have outlasted their shelf life, or because the solvents

have been contaminated or chemically or physically changed.

It should be clear from this discussion that the wastes encompassed by this listing do not include waste streams where the solvent is a contaminant, such that the waste stream is not a spent solvent, as defined above. Thus, wastes which contain as constituents solvents which are used in the industrial process are not included within the scope of this listing. Nor are these waste streams hazardous by virtue of the mixing rule (§261.3(a)(2)(ii)), since a spent solvent is not being mixed with another solid waste.

The Agency, however, does not believe it appropriate to define the term "spent solvent" by using a quantity/volume cut-off (i.e., spent solvents include those solvents which contain x percent or more of solvent). As we have indicated in other support documents (see e.g., Background Document on EP toxicity), the Agency does not presently believe sufficient information exists to establish minimum waste concentration levels for toxic constituents, except for those regulated by the Interim Primary Drinking Water Standards. We intend to make case-by-case determinations via the delisting mechanism to remove those wastes containing minimal concentrations of "spent solvent".

2. Another commenter argued that the scope of the listing of both spent solvents and still bottoms/sludges from the recovery of solvents, is overinclusive because it does not recognize that certain solvent recovery operations produce non-hazardous still bottoms.\* For example, the commenter stated that it is possible to produce a nonleaching, non-ignitable fused waste solid containing as low as 5 percent solvent. Therefore, the commenter recommends that solvent recovery still bottoms be defined as follows:

"Solvent recovery still bottoms: residue from the distillation/evaporation process of recovered solvent which has more than 10% of the original solvent (excluding water) remaining"

The Agency disagrees with the commenter. In the first place, the commenter has not correlated the recommended concentration of solvent with a showing that exposure to these levels of contaminant will not cause substantial hazard. Nor is there documentation for the claim that still bottoms containing 5% of the listed solvent would be incapable of posing substantial harm if mismanaged. Furthermore, the Agency believes that

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\*It should be noted that this comment was directed to waste F004 (the following spent non-halogenated solvents: cresols and cresylic acid, and nitrobenzene; and the still bottoms from the recovery of these solvents). However, EPA's response is also applicable to wastes F001, F002 and F005.

still bottoms containing 5% of the listed solvent may indeed pose a substantial hazard to human health and the environment if improperly managed.\* This premise is based on the following factors:

- (1) The recommended cut-off level (50,000 ppb) is at least an order of magnitude above that needed to cause acute effects, and in most cases orders of magnitude higher (see Appendix A to the listing background document). Thus, still bottoms with 5% concentration of a listed solvent would only have to leach a small percentage of the contained solvent to cause substantial hazard.
- (2) Cresols, cresylic acid and nitrobenzene are all toxic chemicals: nitrobenzene is a suspect carcinogen and has been found to cause a variety of blood disorders from chronic exposure. Cresols and cresylic acid are highly toxic if administered orally and moderately toxic if inhaled. In addition, cresol and cresylic acid may result in damage to the kidney and liver as well as to the central nervous system.
- (3) Because of the toxicity of these solvents, the concentration of solvent in the still bottoms (five percent) is considered significant by the Agency.

\*At a 5 percent level of solvent, the waste streams may no longer be ignitable as defined in §21.21.

- (4) All of these solvents have high or appreciable water solubilities (nitrobenzene: water solubility 1900 mg/l (Appendix B); cresols and cresylic acid: water solubilities 23,500 and 31,000 mg/l (Appendix B) and therefore, could leach into groundwater under improper disposal conditions.
- (5) All of these solvents are likely to persist in groundwater; cresols, cresylic acid and nitrobenzene are not known to hydrolyze while nitrobenzene also does not biodegrade well.\*/

The Agency therefore, believes that still bottoms from the recovery of cresols and cresylic acid, and nitrobenzene may pose a substantial hazard to human health and the environment even when five percent of solvent is in the waste. If an individual generator believes his still bottoms are non-hazardous, the generator should petition the Agency to de-list his waste (see §§260.20 and 260.22).

3. One commenter criticized EPA's generic designation of all spent chlorinated fluorocarbons as hazardous. Therefore, the commenter believes that the broad category (chlorinated fluorocarbons) should be replaced by specific compounds for which documented evidence of hazard is available. The commenter also argued more specifically

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\*These data are all taken from Appendix B to the listing background document.

that trichlorofluoromethane and dichlorodifluoromethane are not hazardous constituents\*/ and that EPA's reason for regulating these materials--that they can rise into the stratosphere and deplete the ozone leading to adverse health and environmental effects--has not yet been proven. The commenter pointed out that the most sophisticated statistical analyses of actual ozone measurements taken at various places around the world have consistently failed to detect the depletion calculated to have occurred to date, despite the fact that the most recent analyses should detect this depletion even if it were only half the calculated amount. The commenter also argued that there have been growing indications that the current ozone depletion theory as it applies to chlorofluorocarbon depletion does not accurately describe the present-day atmosphere, or fails to consider aspects of atmospheric chemistry which are both significant and important. Cited in support is the study Chlorofluorocarbons and Their Effects on Stratospheric Ozone (2nd Rpt.) Pollution Paper No. 15, Department of Environment, Central Directorate on Environmental Pollution, October 1979.

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\*/The commenter cited several reasons for this statement: (1) the Health and Environmental Effects Profile (Appendix A) indicates that both trichlorofluoromethane and dichlorofluoromethane are non-toxic, (2) EPA's proposed action to remove these two compounds from the Clean Water Act toxic pollutant list indicates EPA's admission as to the innocuous nature of these two compounds in the aquatic environment, and (3) EPA's limited discussion of the various factors under §261.11(a)(3) of RCRA indicates that wastes containing these two compounds pose no hazard during storage, transportation, treatment or disposal.

Therefore, the commenter requested that all chlorinated fluorocarbons be deleted from the F001 and F002 generic waste list.

The Agency disagrees with the commenter on both points. With respect to their concern regarding the generic designation of all spent chlorinated fluorocarbons as hazardous, the Agency believes that all chlorinated fluorocarbons share the same physiological and photochemical attributes of concern, namely depletion of the ozone. Therefore, the Agency feels justified in listing the broad category of chlorinated fluorocarbons as hazardous, rather than its individual members.

As to the hazardous nature of the listed chlorofluoromethanes, the Agency agrees that they pose a low potential for adverse acute effects at ambient air concentrations, although there is some indication that long term exposure to very low levels (<400 ppt) will have chronic effects (Health Assessment Document, EPA, October, 1980). In the present instance, however, the Agency's overriding concern relates to the fact that chlorinated fluorocarbons may indirectly cause skin cancer due to the depletion of stratospheric ozone. Such depletion leads to increased intensity of damaging ultraviolet light at the earth's surface. This, in turn, leads to increased skin cancers, reduced productivity of several important agricultural crops and increased

mortality in the larval forms of several important seafood species. The fact that these compounds are proposed to be deleted from the list of toxic pollutants under Section 307(a) of the Clean Water Act does not affect our conclusion, since Section 307 does not address adverse effects arising from air exposure pathways.

The Agency has analyzed the British Ministry of the Environment report and has concluded that there are few differences in regards to the science of CFC transport into the stratosphere and the reactions involving ozone destruction between this report and a recent National Academy of Sciences report which provides the basis for EPA's regulatory action banning the manufacturing, processing and distribution of chlorinated fluorocarbons for those non-essential aerosol propellant uses which are subject to TSCA authority (43 FR 11301, March 17, 1978). While the British Ministry of the Environmental report concluded that ample cause for regulating CFCs does not presently exist, the Agency strongly believes that there is sufficient evidence to regulate and limit chlorinated fluorocarbon emissions. In the judgment of EPA, chlorinated fluorocarbons can be a significant component of a solvent waste stream, can migrate into the environment (stratosphere) if improperly managed, are persistent (remaining intact long enough to migrate to the stratosphere), and may pose a substantial hazard

to human health and the environment. They thus should be regulated as hazardous wastes.\*/ We also note that the Food and Drug Administration (FDA) has promulgated regulations which prohibit the use of chlorinated fluoro-carbons as propellants in containers for products subject to the Federal Food, Drug, and Cosmetic Act.

4. One commenter argued that the "T" (toxic) designation assigned to several of the waste solvents listed under F005, is ill-conceived in light of the information presented in the regulations and in the background documents; specifically, methanol, toluene, methyl ethyl ketone, methyl isobutyl ketone, pyridene and carbon disulfide. More specifically the commenter noted:

Methanol - this compound is not found to be carcinogenic, mutagenic or teratogenic

Toluene - this compound is shown not to be carcinogenic, mutagenic nor teratogenic

Methyl Ethyl - this compound is shown to have  
Ketone no chronic toxicity

Methyl Isobutyl - this compound is shown to have  
Ketone no chronic toxicity

\*/It should be noted that the Office of Toxic Substances/ U.S. Environmental Protection Agency is currently considering further regulation of chlorinated fluorocarbon production and use.

Pyridine - this compound is not carcinogenic  
or mutagenic and the determination  
of teratogenicity is questionable

Carbon disulfide - this compound is shown to have  
no chronic toxicity

Therefore, the commenter recommends that these compounds  
no longer be designated as toxic wastes.

The Agency continues to believe that all of these  
spent solvents, with the exception of methanol and methyl  
isobutyl ketone should continue to be listed as toxic.  
In reviewing the data available in the record, the  
Agency believes that there is sufficient evidence to  
continue to list these solvents as "toxic" wastes  
(except for methanol and methyl isobutyl ketone). As  
explained in the health and environmental effects section  
of the listing background document, "Waste from usage of  
organic solvents" as well as the respective Appendix A  
health profiles for these compounds, it has been reported  
that chronic low level exposure to toluene has caused  
chromosome damage in humans and has led to the development  
of neuro-muscular disorders. Toluene has also been  
reported to cause reproductive problems to female workers  
during occupational exposure.

Methyl ethyl ketone (MEK), although only moderately  
toxic via ingestion, can affect the peripheral nervous  
system and is an experimental teratogen. In addition,  
lethal doses in animals caused marked congestion of  
the internal organs and slight congestion of the brain.

Chronic exposure to pyridine has produced liver and kidney damage in both animals and humans. In addition, small doses of pyridine have produced tremors and ataxia, irritation of the respiratory tract with asthmatic breathing and paralysis of the eye muscles, vocal cords and bladder.

Chronic exposure to carbon disulfide can affect the cardiovascular and central nervous system, causing personality changes. In addition, exposure to short term, but high atmospheric concentrations can lead to narcosis and death. Carbon disulfide is also suspected of being teratogenic. Therefore, these solvents will continue to be listed as toxic.

The Agency, however, agrees with the commenter that both spent methanol and methyl isobutyl ketone were improperly listed as toxic wastes. Methanol's oral toxicity is rated as low<sup>\*</sup> and in fact is permitted in foods for human consumption as an additive. Methyl isobutyl ketone's principal toxic effects appears to be irritation of the eyes and mucous membranes, and gastrointestinal upset. Under these circumstances, we do not believe a toxicity listing for these solvents is appropriate, thus, the Agency will no longer list spent methanol and methyl isobutyl ketone as toxic wastes. However, both methanol and methyl isobutyl ketone are ignitable (flash points

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<sup>\*</sup>/ Saw, V. Irving. Dangerous Properties of Industrial Materials. 5th ed. Van Nostrand Reinhold Co. New York. 1979

of 54°F and 61°F, respectively). Thus spent methanol and methyl isobutyl ketone will continue to be listed as ignitable hazardous wastes.

5. One commenter criticized the Agency's determination that chlorobenzene, o-dichlorobenzene, methanol, toluene, methyl ethyl ketone, methyl isobutyl ketone, isobutanol and ethyl benzene are persistent and do not degrade well. The commenter argued that this inclusion is contrary to the published literature, including this Agency's own studies, which shows that biodegradation is the preferred method of treatment for these compounds in aqueous solutions. The commenter therefore, believes that the degradation data within the listing background document should be reviewed and properly assessed in listing.

We note initially that the commenter's claims are largely unsubstantiated. We note further that biodegradation plays a limited role in the environmental persistence of the waste constituents because groundwater, the exposure pathway of paramount concern, is abiotic. As pointed out in the listing background document (pp. 57-61), a number of these solvents have migrated via air and groundwater pathways, and persisted for long periods of time, and caused substantial hazard in the course of actual waste management practice. Thus,

chlorobenzene, o-dichlorobenzene, toluene and methyl ethyl ketone have all been detected in basement air, sump pumps and/or in solid surface samples in the Love Canal area.\*/ All of these solvents (chlorobenzene, o-dichlorobenzene, toluene and methyl ethyl ketone) are thus demonstrably persistent enough to have migrated from a disposal site and contaminate adjacent areas to create a substantial hazard.

In addition, the following properties/characteristics of these compounds indicate further the persistence of these solvents:\*\*/

chlorobenzene - this solvent is not amenable to hydrolysis nor does it biodegrade very well and therefore is expected to persist in the environment.

toluene - this solvent is persistent in abiotic environments (such as most aquifers) and therefore is expected to persist in groundwater. Toluene also is relatively soluble (water solubility 470 mg/l at 25°C), and thus would be expected to migrate into groundwater.

methyl ethyl ketone - this solvent, in addition to being reported at Love Canal, has been detected at several sites near groundwater

\*/ Since methanol and methyl isobutyl ketone are no longer being considered toxic, a discussion on their persistence is no longer appropriate.

\*\*/ These data are all taken from the listing background document, "Waste from usage of organic solvents".

contaminated by an old chemical company dump, again showing migratory potential and persistence.\*/

With respect to isobutanol, the Agency has not made any claim as to the persistence of this compound; however, due to its toxicity and extremely high water solubility (water solubility 95,000 mg/l at 18°C), the Agency believes that this solvent may pose a substantial hazard to human health and the environment if improperly managed.

Finally, ethyl benzene is being listed because of its ignitability hazard, not toxicity. As is indicated in the regulations (§261.21, 45 FR 33121-33122, May 19, 1980), a liquid waste is considered ignitable, and therefore hazardous, if it has a flash point less than 140°F. Consequently, the persistence of ethyl benzene is not at all relevant.

Therefore, absent any information provided by the commenter on the persistence and degradability of these solvents, the Agency finds no reason to change its original conclusions.

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\*/Listing Background Document, "Wastes from usage of organic solvents", Section IV. B. (Migratory potential and persistence of halogenated and non-halogenated solvents) pg. 31.

6. One commenter criticized the Agency's conclusion, as stated in the listing background document, that "the solubility of these solvents is uniformly high " (LBD pg. 3) and "the solubility in water of these halogenated solvents is quite high" (LBD pg. 14) when in fact, as the commenter points out, their solubilities vary from 10 to 20,000 mg/l (LBD pg. 55). The commenter went on to argue that the Agency's determination that "these high solubilities demonstrate a strong propensisty to migrate from inadequate land disposal facilities in substantial concentrations" (LBD pg. 15) and "all of these waste solvents have significant potential for migration, mobility and persistence..." (LBD pg. 52) is overstated when in fact, as the commenter indicates, migration, mobility and persistence differ significantly with respect to both routes of transport and rates of degredation. Therefore, the commenter believes that the Agency needs to reassess these listings.

The Agency agrees with the commenter that the water solubilities of the chlorinated hydrocarbons do vary considerably. However, in re-evaluating the data, the Agency believes that the solubilities of all of these solvents except 1,1,2-trichloro-1,2,2-trifluoroethane are generally high and do indeed indicate a potential for migration from inadequate land disposal facilities.\*/

\*/Although the water solubility for trichlorofluoromethane is high, the principal concern with this solvent is its potential to rise to the stratosphere where it may release chlorine atoms and deplete the ozone.

The Agency recognizes that solubility is not the sole parameter which determines the potential of a substance to migrate into the environment, i.e., mobility and persistence also play a role. However, it is a key parameter in evaluating how likely these substances are to migrate from land disposal facilities. Indeed, this potential to migrate has been demonstrated for all of these solvents, except methylene chloride, in actual damage cases, i.e., tetrachloroethylene, trichloroethylene, 1,1,1-trichloroethane, chlorobenzene and o-dichlorobenzene have all been detected to migrate at Love Canal or other disposal facilities. Methylene chloride, although not detected at any disposal facilities, is highly soluble with a water solubility of 20,000 mg/l at 25°C, and thus has the potential to migrate from disposal sites and create a problem. However, the Agency has modified the listing background documents as to the solubilities of these solvents to better reflect the Agency's conclusions.

With respect to the solvent 1,1,2-trichloro-1,2,2-trifluoroethane, the Agency has indicated clearly that the potential to migrate and contaminate groundwater is not of concern. The primary hazard posed by the mismanagement of this solvent, as with all chlorinated fluorocarbons, is the potential to rise to the stratosphere and indirectly cause skin cancer due to the

depletion of stratospheric ozone\*/ (see Response to Comments No. 3 of this document for a more detailed discussion).

The Agency also agrees that its conclusions regarding migration, mobility and persistence are overstated. Therefore, the listing background documents have been changed to reflect the Agency's determination that, while the various chlorinated solvents do differ in their migratory potential, mobility and persistence, they all may pose a substantial present or potential hazard to human health and the environment, if improperly managed, when considering the routes and rates of transport and degrees and rates of degradation.

7. One commenter believed that the Agency's decision to include trichloroethylene on the list of chemicals which have demonstrated substantial evidence of carcinogenicity was inaccurate. The commenter indicated that according to Elizabeth Weisberger of the National Institute of Health, whose organization did the original studies which classified trichloroethylene as a "merely suspicious carcinogen", indicated that "trichloroethylene seems not to be a carcinogen." The commenter also argued that more extensive and recent research indicates that

\*/1,1,2-trichloro-1,2,2-trifluoroethane is considered to be extremely volatile (vapor pressure - 270 mm of Hg at 20°C), and thus is likely to rise into the atmosphere.

trichloroethylene may not be carcinogenic after all.

The Agency disagrees with the commenter. Trichloroethylene has been designated carcinogenic by EPA's Cancer Assessment Group (CAG) after reviewing the available data in the literature. In fact, before a chemical compound is deemed carcinogenic by CAG, it is subject to exhaustive literature study and evaluation. In light of CAG's determination, EPA will continue to include trichloroethylene as a chemical which has demonstrated substantial evidence of carcinogenicity.

8. One commenter questioned the Agency's characterization of 1,1,1-trichloroethane as a suspect carcinogen. The commenter argued that 1,1,1-trichloroethane has not been found to be a carcinogen. They quote the NCI Bioassay of 1,1,1-Trichloroethane for Possible Carcinogenicity (January 1977), which states:

"A variety of neoplasms were represented in both 1,1,1-trichloroethane treated and matched-control rats or mice. However, each type of neoplasm has been encountered previously as a lesion in untreated rats or mice. The neoplasms observed are not believed attributable to 1,1,1-trichloroethane exposure, since no relationship was established between the dosage groups, the species, sex, type of neoplasm or the site of occurrence. Even if such a relationship were inferred, it would be inappropriate to make an assessment of carcinogenicity on the basis of this test, because the abbreviated life spans of the rats and the mice."

The commenter also argued that EPA's own Office of Drinking Water, in their appendices to Planning Workshops to

Development Recommendations for a Groundwater Protection Strategy, state that methyl chloroform (1,1,1-trichloroethane) is not considered to be a carcinogen (June 1980). Therefore, the commenter believes that there is no support for the carcinogenicity of 1,1,1-trichloroethane and argues that it be deleted from all lists of hazardous wastes.

The Agency disagrees with the commenter's claim. Although the NCI Bioassay Study on the carcinogenicity of 1,1,1-trichloroethane referred to in the listing background document (pg. 464) and an unpublished study are inconclusive, positive responses in two in vitro systems (a rat embryo cell transformation assay (Price et. al. 1978, Transforming Activities of Trichloroethane and Proposed Industrial Alternatives. In vitro. 14:290.) and a bacterial mutation assay (Simmon et. al. 1977. Mutagenic activity of chemicals identified in drinking water, In: Progress in Genetic Toxicology, ed. I.D. Scott, B. A. Bridges and F. H. Sobels, pp. 249-258; McCann, J. and B. Ames, 1976. Detection of carcinogens as mutagens in the Salmonella microsome test: Assay of 300 chemicals. Proc. Nat. Acad. Sci. 78:950.)) currently used to detect chemical carcinogens, indicate that 1,1,1-trichloroethane has the potential for carcinogenicity in animals (App. A). Additionally, a two year carcinogenesis animal bioassay

is being repeated at the National Cancer Institute. Therefore, the Agency believes that there is ample evidence to consider 1,1,1-trichloroethane as a suspect carcinogen<sup>\*</sup>/, and thus will continue to include 1,1,1-trichloroethane as a constituent of concern.

9. One commenter also argued that the statements in the background document that "methylene chloride is<sup>o</sup> reported as being mutagenic to a bacterial strain, S. typhimurium", and "methylene chloride... is highly mutagenic" are inaccurate. The commenter pointed out that a variety of more detailed tests performed subsequently and not cited in the listing background document prove otherwise. For example, a definitive cell transformation test for methylene chloride was found negative. Additionally, many other tests have been run for carcinogenicity of methylene chloride with negative results.

The Agency agrees. The current assessment on the carcinogenicity of methylene chloride is only based on animal experiments which are so far incomplete. However, methylene chloride is the subject of an NCI sponsored bioassay. In addition, EPA has found "suggestive" evidence of the carcinogenicity of methylene chloride

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<sup>\*</sup>/It should be noted that the Agency recently determined to retain the listing of 1,1,1-trichloroethane as a toxic pollutant under §307(a) of the Clean Water Act. The reasons for that action are incorporated by reference herein.

(App. A). The Agency cannot ignore this information. Therefore, the listing background document will be revised to indicate that methylene chloride is only a "suspect" carcinogen.

10. One commenter questioned the Agency's characterization of tetrachloroethylene, methylene chloride, trichloroethylene and 1,1,1-trichloroethane as aquatically toxic. The commenter indicated that statements relative to methylene chloride like "acute toxicity values range from 147,000 to 310,000 mg/l (correct units are ug/l) for aquatic organisms" are meaningless until put into relative significance. When compared with most common nonhalogenated solvents, the commenter argues, the halogenated solvents were less toxic to the tested fish species. In addition, the commenter pointed out that EPA, in fact, concurs with this viewpoint by stating, "aquatic organisms tend to be fairly resistant to dichloromethane (methylene chloride), with acute values ranging from 193,000 to 331,000 ug/l (EPA BD 38 at 389). Therefore, the commenter believes that EPA has not properly assessed the relatively low aquatic toxicities of these halogenated solvents.

In re-evaluating the aquatic toxicity of tetrachloroethylene, methylene chloride, trichloroethylene and 1,1,1-trichloroethane, the Agency agrees with the commenter that all four of these halogenated solvents are not of regulatory concern under the hazardous waste program to

warrant characterization as "aquatically toxic." In the Registry of Toxic Effects (1975 Edition), a widely used reference book which is published by the National Institute for Occupational Safety and Health (NIOSH), a rating of the aquatic toxicity or non-toxicity of chemical substances is provided. In this rating, substances with an LC<sub>50</sub> value of between 10,000 ug/l to 100,000 ug/l is considered slightly toxic while substances with an LC<sub>50</sub> value above 100,000 ug/l is practically non-toxic. Based upon this rating, methylene chloride is practically non-toxic while the other halogenated solvents are slightly toxic. Therefore, the Agency will modify the listing background document to reflect this change. However, it should be noted that toxic wastes are not so designated solely on the basis of their aquatic toxicity. As discussed earlier, all of these halogenated solvents exhibit other toxic effects i.e., carcinogenicity, chronic toxicity, etc. which are sufficient to warrant designation of these solvents as toxic.

11. One commenter also argued that the Agency has misinterpreted and overstated the bioaccumulation potential for both the halogenated and non-halogenated solvents, arguing that most of these solvents have a low bioaccumulation potential. In particular, the commenter believes that the Agency has shown a lack of perspective by

concluding that, "...methanol could bioaccumulate causing numerous adverse health effects from prolonged and/or repeated exposure" (EPA BD-11 at 59), despite its reported very low  $K_{ow}$  of 5 and readily biodegradable. Therefore, the commenter believes that the bioaccumulation data should be reviewed and properly assessed in listing.

As discussed in the preamble to Part 261 of the hazardous waste regulations (45 FR 33106-33107), the Agency in listing wastes for which a characteristic has not been developed has adopted a flexible, multiple factor approach to be better able to accommodate itself to the complex determinations of hazard. These multiple factors include the type of toxic threat posed, the concentrations of the toxic constituents in the waste, the migratory potential, persistence and degradation of the toxic constituents, the degree to which the toxic constituents bioaccumulate in ecosystems, the plausible types of improper management to which the waste could be subjected, the quantities of waste generated, and other factors not explicitly designated by the Act. Thus, if a substance exhibits one or more of these properties, the Agency may list the waste as hazardous. The bioaccumulation potential of a substance is not considered by the Agency as a necessary factor before a waste can be listed. Therefore, just because a chemical substance is not bioaccumulative

is no reason not to list a waste.

With respect to the commenter's claim for methanol, the Agency is no longer listing this solvent for toxicity, but for ignitability. Bioaccumulative propensity of this compound thus is no longer relevant.

12. One commenter cited some inconsistencies/errors in the listing background documents and suggested that the Agency make the appropriate revisions.

The Agency agrees. There were some typographical and transcription errors, e.g., in the methylene chloride background document, as well as some judgmental errors. Therefore, within the limits of its resources, the Agency has made every effort to correct such errors.

13. One commenter criticized the Agency's conclusion as stated in the listing background document that, "the chlorinated waste hydrocarbons are toxic" (EPA BD-11 at 3) when in fact, as the commenter points out, that the oral-rat LC<sub>50</sub> values vary by several orders of magnitude. Therefore, the commenter believes that the listing of these halogenated solvents are not fully warranted in all cases.

The Agency strongly disagrees with the commenters unsubstantiated claim. As discussed in the preamble to the May 19, 1980 hazardous waste regulations (45 FR 33107), the Agency listed a number of toxic wastes

as those "which have been shown inreputable scientific studies to have toxic, carcinogenic, mutagenic or teratogenic effects on humans or other life forms." Toxicity is defined to include systemic effects of chronic low level exposure, acutely toxic<sup>\*</sup>/, aquatic toxicity, phytotoxicity or the potential (as with chlorinated fluorocarbons) for indirectly causing harm to human health or other life forms. Therefore, a substance with a high LC50 value is not necessarily non-toxic.

In reviewing the data available in the record<sup>\*\*</sup>/, the Agency is convinced that these substances are properly designated as toxic, and that improper management and disposal of these waste solvents may pose a substantial present or potential hazard to human health and the environment. Since the commenter failed to provide additional toxicity data except as discussed in other parts to this section, the Agency finds no reason to change its original conclusion to list these solvents as toxic wastes.

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<sup>\*</sup>/Acutely toxic does not include those wastes which are defined in §261.11(a)(2) as acutely hazardous.

<sup>\*\*</sup>/Appendix A (Health and Environmental Effects Profiles) outlines the health and environmental effects exhibited by each of these compounds.

## Electroplating and Metal Finishing Operations

Wastewater Treatment Sludges From Electroplating Operations except from the following processes: (1) sulfuric acid anodizing of aluminum; (2) tin plating on carbon steel; (3) zinc plating (segregated basis) on carbon steel; (4) aluminum or zinc-aluminum plating on carbon steel; (5) cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel; and (6) chemical etching and milling of aluminum (T)

Wastewater Treatment Sludges from the Chemical Conversion Coating of Aluminum (T)\*

### Summary of Basis for Listing

Wastewater treatment sludges from electroplating operations are generated by a number of industry categories located nationwide. These wastes contain a variety of metals such as chromium, cadmium, nickel, and also contain complexed cyanides. The Administrator has determined that solid wastes from these processes may pose a substantial present or potential hazard to human health and the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

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\*In response to comments, this listing has been modified to better define those electroplating operations which generate hazardous waste - see Response to Comments in back of the background document for additional details.

Chemical conversion coating of aluminum is included in the general category of electroplating, however, since this waste is being listed only for the presence of chromium and cyanide, the waste will be listed separately.

1. Wastewater treatment sludges from the listed electroplating operations contain significant concentrations of the toxic metals chromium, cadmium and nickel and toxic complexed cyanides.
2. Wastewater treatment sludges from the chemical conversion coating of aluminum contain significant concentrations of chromium, a toxic metal and complexed cyanides.
3. Leaching tests using the extraction procedure specified in the extraction procedure toxicity characteristic have shown that these metals leach out in significant concentrations, with some samples failing the extraction procedure toxicity characteristic. Therefore, the possibility of groundwater contamination via leaching will exist if these waste materials are improperly disposed.
4. A large quantity of this waste is generated annually with amounts expected to increase substantially when the pretreatment standards for these sources become effective.
5. Damage incidents (i.e., contaminated wells, destruction of animal life, etc.) that are attributable to the improper disposal of electroplating wastes have been reported, thus indicating that the wastes may be mismanaged in actual practice, and are capable of causing substantial harm if mismanagement occurs.

#### Sources of the Waste and Typical Disposal Practices

The electroplating industry consists of both job shops and captive platers. Job shops are small, independent operations performing electroplating on a contract basis while captive facilities are part of an integrated manufacturing firm (i.e., electroplating operations carried-out in an automobile manufacturing facility, aircraft manufacturing facility, etc.). Of the approximately 10,000 electroplating facilities in the

United States, it is estimated that 3,000 are job shops and 6,100 are captive shops including 400 printed circuit board manufacturers. Approximately 7 percent of the job shops and 42 percent of the captive shops discharge directly to the waters of the United States.(1)

#### Process Description

Electroplating, as defined in this document, includes a wide range of production processes which utilize a large number of raw materials. Production processes include common and precious metals electroplating, anodizing, chemical conversion coating (i.e., coloring, chromating, phosphating and immersion plating), electroless plating, chemical etching and milling and printed circuit board manufacturing (5). The primary purpose of electroplating operations is to apply a surface coating, typically by electrode decomposition, to provide protection against corrosion, to increase wear or erosion resistance, or for decorative purposes. The operation itself involves immersing the article to be coated/plated into a bath consisting of acids, bases, salts, etc. A plating line is a series of unit operations conducted in sequence in which one or more coatings are applied or a basis material is removed. Figure 1 illustrates a standard electroplating process. (For a more detailed discussion of the electroplating process, see the Development Document for Existing Source Pretreatment Standards for the Electroplating Point Source Category, August 1979 (5).)

The metals used in electroplating operation (both common and precious metal plating) include cadmium, lead, chromium in hexavalent form, copper, nickel, zinc, gold and silver. Cyanides are also extensively used in plating solutions and in some stripping and cleaning solutions. Electroless plating often uses copper, nickel and tin complexed with cyanide. Etching solutions are commonly made up of strong acids or bases with spent etchants containing high concentrations of spent metal. The solutions include ferric chloride, nitric acid, ammonium persulfate, chromic acid, cupric chloride and hydrochloric acid. Anodizing is usually performed on aluminum parts using solutions of sulfuric or chromic acid often followed by a hot water bath, however, nickel acetate or sodium or potassium dichromate seal may also be used in the process.

Chemical conversion coating processes apply a coating to the previously deposited metal or basis metal for increased corrosion protection, lubricity, preparation of the surface for additional coatings or formulation of a special surface appearance. This manufacturing operation includes chromating, phosphating, metal coloring, and immersion platings.(5) During the process of chromating, a portion of the base metal is converted to one of the components of the surface films by reaction with aqueous solutions containing hexavalent chromium (CrVI). The solutions are generally acidic and

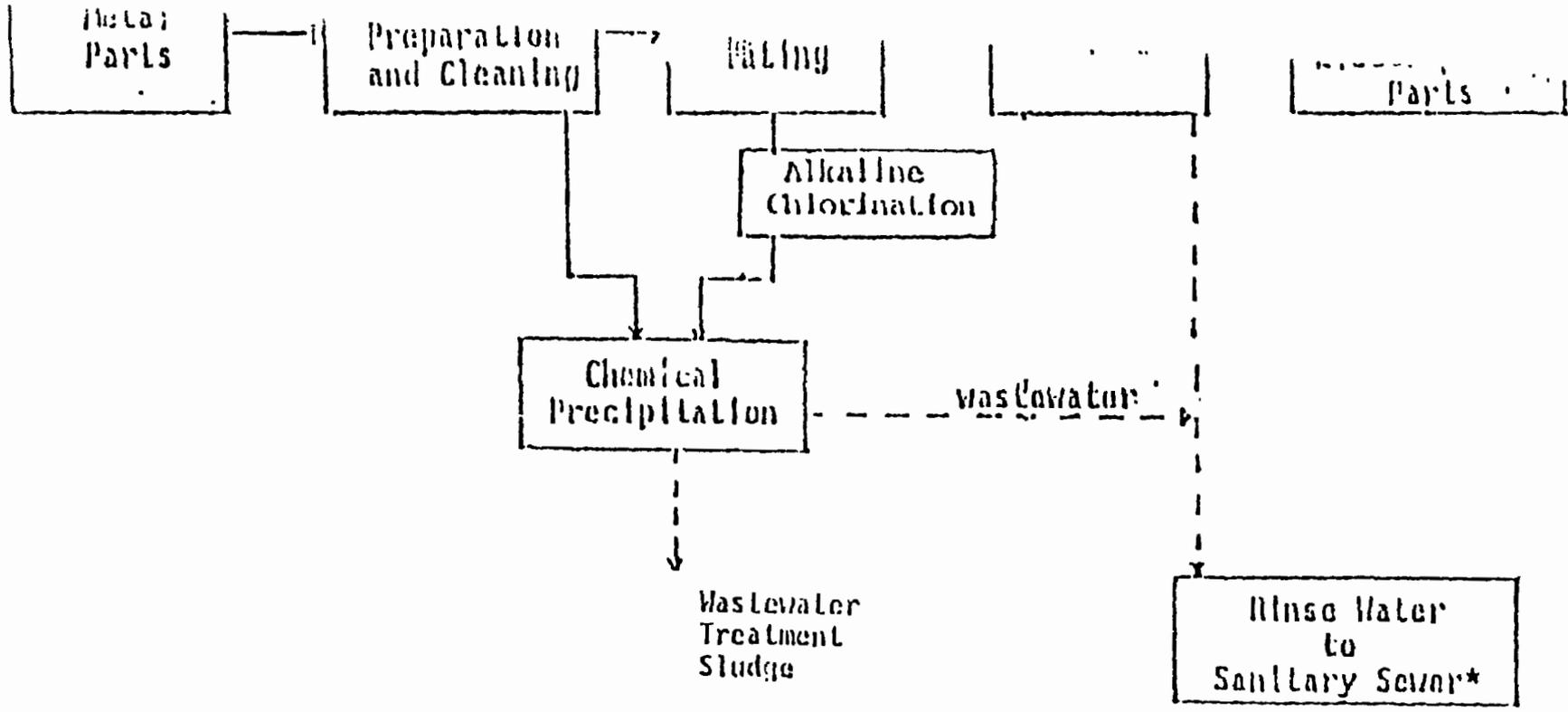


FIGURE 1 TYPICAL ELECTROPLATING PROCESS

Immersion tin plating baths contain stannous chloride, potassium bitartrate, ammonium aluminum sulfate, sodium cyanide or sodium hydroxide. Typical immersion gold plating used to gild inexpensive items of jewelry uses solutions of gold chloride, potassium cyanide, or pyrophosphate. Typical process baths used in the industry are shown in Table 1.(7)

#### Waste Generation and Composition

As indicated in Figure 1, the spent plating/coating solution and rinse water is chemically treated to precipitate out the toxic metals and to destroy the cyanide. The extent to which plating solution carry-over adds to the wastewater and enters the sludge depends on the type of article being plated and the specific plating method employed.

The composition of these sludges will vary because of the multitude of production processing sequences that exist in the industry. For example, printed circuit board manufacture involves electroplating, etching, electroless plating and conversion coating, and generate one type of sludge. A different processing sequence, on the other hand, generates a sludge with a differing composition. However, it is expected that since most platers conduct a number of different electroplating operations, most of the sludges will contain significant concentrations of toxic metals, and may also contain complexed cyanides in high concentrations if cyanides are not properly isolated in the treatment process.

Table 1<sup>(7)</sup>

Typical Electroplating Baths and Their Chemical Composition

<u>Plating Compound</u>	<u>Constituents</u>	<u>Concentration (g/l)</u>
1. Cadmium Cyanide	Cadmium oxide	22.5
	Cadmium	19.5
	Sodium cyanide	77.9
	Sodium hydroxide	14.2
2. Cadmium Fluoborate	Cadmium fluoborate	251.2
	Cadmium (as metal)	94.4
	Ammonium fluoborate	59.9
	Boric acid	27.0
	Licorice	1.1
3. Chromium Electroplate	Chromic acid	172.3
	Sulfate	1.3
	Fluoride	0.7
4. Copper Cyanide	Copper cyanide	26.2
	Free sodium cyanide	5.6
	Sodium carbonate	37.4
	Rochelle salt	44.9
5. Electroless Copper	Copper nitrate	15
	Sodium bicarbonate	10
	Rochelle salt	30
	Sodium hydroxide	20
	Formaldehyde (37%)	100 ml/l
6. Gold Cyanide	Gold (as potassium gold cyanide)	8
	Potassium cyanide	30
	Potassium carbonate	30
	Depotassium phosphate	30
7. Acid Nickel	Nickel sulfate	330
	Nickel chloride	45
	Boric acid	37
8. Silver Cyanide	Silver cyanide	35.9
	Potassium cyanide	59.9
	Potassium carbonate (min.)	15.0
	Metallic silver	23.8
	Free cyanide	41.2
9. Zinc Sulfate	Zinc sulfate	374.5
	Sodium sulfate	71.5
	Magnesium sulfate	59.9

Table 2 illustrates the varying composition of these sludges for two of the metals in twelve different plating processes.

There are a number of electroplating operations, however, which are usually conducted separately and which are not expected to contain significant concentrations of the toxic metals or cyanides. These processes (tin plating on carbon steel, zinc plating (segregated basis) on carbon steel, aluminum or zinc-aluminum plating on carbon steel, cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel, sulfuric acid anodizing of aluminum and chemical etching and milling of aluminum), therefore, have been excluded from the general category of electroplating operations. Wastewater treatment sludges generated from these processes are consequently not listed hazardous wastes, but may be hazardous if they fail one of the characteristics.

The predominant type of wastewater treatment sludge generated from this industry is metal hydroxide sludge (which results from alkaline precipitation). Those electroplating processes using chromium all employ the hexavalent form of this element. Consequently the raw wastes resulting from this process contain chromium only in the hexavalent form. The efficiency of the removal of hexavalent chromium depends on the extent of its reduction. If reduction is incomplete, or if neutralization and metal precipitation take place too rapidly, hexavalent chromium is likely to be entrained in

Table 2  
Heavy Metal Content for Chromium, and Cadmium  
in Electroplating Sludges-Dry Weight<sup>(4)</sup>

<u>Primary Plating Process</u>	<u>Cr</u>	<u>Cd</u>
Segregated Zinc	200	<100
Segregated Cadmium	62,000	22,000
Zinc Plating and Chromating	65,000	1,100
Copper-Nickel-Chromium on Zinc	500	ND
Aluminum Anodizing* (chromic process)	1,700	ND
Nickel-Chromium on Steel	14,000	-
Multi-Process Job Shop	25,000	1,500
Electroless Copper on Plastic, Acid Copper, Nickel Chromium	137,000	ND
Multi-Process with Barrel or Vibratory Finishing	570	-
Printed Circuits	3,500	<100
Nickel-Chromium on Steel	79,200	<100
Cadmium-Nickel-Copper on Brass and Steel	48,900	500

the precipitation sludges, resulting in their contamination with hexavalent chromium. Moreover, the higher the concentration of hexavalent chrome in the wastewater, the greater is the likelihood of its inefficient or ineffective reduction, and the consequent likelihood of the contamination of chromium hydroxide sludges with hexavalent chrome. Screening studies have shown CrVI concentrations averaging 420 ppm in raw waste streams from electroplating (metal finishing) operations.<sup>(14)</sup> Values as high as 12,900 ppm have been reported.<sup>(14)</sup> In fact, sampling data show that concentrations of hexavalent chromium in raw waste from metal finishing operations and chromium concentrations in the effluent after wastewater treatment are positively correlated (ref. 14, p. VII-27), showing that inefficient reduction does occur. Although not widely used, when wastewater is treated by sulfide precipitation, metallic sulfide sludges, are also generated.

Among those facilities which discharge to publicly owned treatment works (POTW's), approximately 80 percent of the job shops and 70 percent of the captive shops do not presently treat their wastewater and, therefore, do not currently generate water pollution control sludges. However, compliance with the electroplate pretreatment standards for existing job shops will be required by October 1982, and for captives shortly thereafter. Thus, when the regulations are implemented, virtually all electroplaters will generate a sludge and drastically increase the quantity of wastewater treatment sludge produced (see page 14 below).

### Typical Disposal Practices

A recent study (2), surveying 48 plants, indicated that approximately 20 percent of the electroplating facilities dispose of their waste on-site while the remaining 80 percent haul their waste off-site to commercial or municipal disposal facilities. The actual disposal practices utilized by the industry vary greatly (i.e., landfilling, lagooning, drying beds and drum burial). However, the Agency is aware that electroplating facilities are known to be using extremely poor hazardous waste disposal practices. For example, one printed circuit board manufacturer is known to dispose of its waste sludges in a dry river bed.(8) Numerous damage incidents caused by industry waste disposal practices likewise indicates poor waste management practices.

### Hazards Posed by the Waste

As indicated earlier in Table 2 and as shown in Table 3, wastewater treatment sludge from electroplating facilities generating a listed waste contain significant concentrations of the toxic metals cadmium, chromium and nickel (with some levels exceeding 1,000 mg/kg (dry weight)) and cyanide. Table 4 provides some additional analytical data on the composition of raw wastewater from forty-six coatings plants. As is indicated, these toxics are present in the raw wastewater, and thus can be expected to be found in the treatment sludge at significant levels, particularly after implementation of the electroplating industry pretreatment standards. In the

sludges the metallic elements occur as hydroxides. As outlined above, chromium may be present as the entrained hexavalent species.

Leaching tests run by the American Electroplaters' Society (AES) under a grant from the Industrial Environmental Research Laboratory (IERL) U.S. Environmental Protection Agency have shown that these metals leach out in significant concentrations with some samples failing the extraction procedure toxicity characteristic (Table 5). The leaching tests used in the AES study were performed on twelve separate samples using the proposed extraction procedure (43 FR 58956-58957). A leaching test was also performed on two samples using the ASTM distilled water leaching test; the results of this test (Table 6) indicate that two of the contaminants of concern (i.e., chromium and cadmium) may not solubilize in water to the extent found in the acid leaching test. However, since these sludges tend to be disposed of in acid environments (i.e. sanitary landfills), the acid leach test would replicate more closely what would be expected to happen under field conditions, and thus is more predictive of potential hazards from improper management. Cyanides have also been shown to leach from these wastes at concentrations ranging from 0.5 to 170 mg/l.<sup>(6)</sup> The Public Health Service's recommended concentration limit for cyanide in drinking water is 0.2 mg/l<sup>(12)</sup>, indicating that cyanide leaching may also lead to a substantial hazard.

Table 3

Projected Sludge Concentrations For Various Heavy  
Metals and Cyanides (mg/l) (5)\*

<u>Pollutant</u>	<u>Raw Waste Conc. (mean)</u>	<u>Projected Sludge Conc. (mean)</u>	
		<u>2% Solids</u>	<u>20% Solids</u>
Cadmium	0.08	3.2	32.5
Nickel	5.0	486.2	4862.0
Chromium, Total	3.8	369.7	3697.0
Cyanide, Total	0.4	42.9	429.2

\*Projections of sludge concentrations are based on mean raw waste sampled during an effluent guidelines study. This study utilized an 82 plant data base and the data are derived from analyses of actual raw waste concentration, assumptions of clarifier removal efficiencies (96-98%) and non-dewatered and dewatered sludge solids content (2% and 20%, respectively). To estimate pollutant concentrations in sludge, the assumption is made that:

1. 1% of the influent flow goes to the sludge stream at 2% solids.
2. The clarifier removal efficiencies were 96-98%.

Therefore,

$$\text{Mass removed} = \text{influent flow} \times \text{influent waste concentration} - (1-.01) \times \text{influent flow} \times \text{effluent concentration}$$

And,

$$\text{Sludge pollutant concentration} = \frac{\text{mass removed}}{.01 \times \text{influent flow}}$$

Table 4

Composition of Raw Waste Streams From Coating

Processes (mg/l)(15)

Chromium, total	.19 - 79.2
Cyanide, total	.005 - 126.0
Cyanide, amenable to chlorination	.004 - 67.56

Table 5

Extract Concentrations From Electroplating Wastewater  
Treatment Sludge (mg/l)<sup>(4)</sup>

<u>Primary Plating Process</u>	<u>Cr*</u>	<u>Cd*</u>
1A Segregated Zinc	1.22	0.23
2A Segregated Cadmium	1.89	<u>126</u>
3A Zinc Plating and Chromating	<u>85.0</u>	<u>6.0</u>
4A Copper-Nickel-Chromium on Zinc	<u>21.8</u>	-
5A Aluminum Anodizing	<0.01	-
6A Nickel-Chromium on Steel	<u>25.4</u>	-
7A Multi-Process Job Shop**	<u>0.24</u>	<u>2.16</u>
8A Electroless Copper on Plastic, Acid Copper, Nickel, Chromium	<u>400</u>	-
9A Multi-Process with Barrel or Vibratory Finishing**	0.32	0.03
10A Printed Circuits	0.12	-
11A Nickel-Chromium on Steel	4.22	<0.01
12A Cadmium-Nickel-Copper on Brass and Steel	4.85	<u>268</u>

Note: Those concentrations underlined would fail the Extraction Procedure Toxicity Characteristic

\* These values were determined using the proposed extraction procedure contained in the toxicity characteristic.

\*\* The ASTM distilled water extraction procedure was run on these samples with the following results:

<u>Plant</u>	<u>Cr (mg/l)</u>	<u>Cd (mg/l)</u>
7A	0.63	0.03
9A	0.04	

Once released from the matrix of the waste, cadmium, hexavalent chromium, nickel, and cyanide could migrate from the disposal site to ground and surface waters utilized as drinking water sources. Hexavalent chromium compounds, both chromates and dichromates have extremely high water solubility (see Attachment II). Therefore hexavalent chrome, if present in these wastes, will leach into groundwaters and effluent streams, and is likely to pollute such waters in amounts significantly exceeding the NIPDWS of .05 mg/l.

Present practices associated with the landfilling, dumping or impounding of the waste may be inadequate to prevent such occurrences. For instance, selection of disposal sites in areas with permeable soils can permit contaminant-bearing leachate from the waste to migrate to groundwater. This is especially significant with respect to lagoon disposed wastes because a large quantity of liquid is available to percolate through the solids and soil beneath the fill. Actual damage incidents involving electroplating wastes are presented in Attachment I, again showing that actual mismanagement of electroplating wastes has occurred, and has resulted in substantial environmental hazard.

The prevalence of off-site disposal creates a further potential for mismanagement and substantial hazard. Not only is there a danger of mismanagement in transport, but there is the further danger of unmanifested wastes never reaching their destination or of being disposed with incompatible wastes.

An overflow with respect to lagoon disposed wastes might be encountered if the liquid portion of the waste is allowed to reach too high a level in the lagoon; a heavy rainfall could cause flooding which might reach surface waters in the vicinity unless the facility has proper diking and other flood control measures.

In addition to difficulties caused by improper site selection, unsecure land disposal facilities are likely to have insufficient leachate control practices. There may be no leachate collection and treatment system to diminish leachate percolation through the wastes and soil underneath the site to groundwater and there may be no surface run-off diversion system to prevent contaminants from being carried from the disposal site to nearby surface waters.

With regard to the fate of these waste constituents once they migrate, the heavy metal contaminants present in the waste are elements which persist indefinitely in some form and therefore may contaminate drinking water sources for long periods of time. Cyanides have been shown to be extremely mobile in the soil environment<sup>(9)</sup> and have been shown to move from soils to groundwater.<sup>(10)</sup> Thus cyanide is also available for potential release and transport to environmental receptors.

The Agency has determined to list wastewater treatment sludges from electroplating operations as T hazardous wastes, on the basis of chromium, cadmium, nickel and cyanide, although

chromium and cadmium are also measurable by the (E) characteristic. Moreover, concentrations for chromium and cadmium in the EP extract from this waste from individual sites might be less than 100 times the national interim primary drinking water standard as indicated (although the Agency's own extraction data indicates that extract concentrations have exceeded the 100 x benchmark for some generators). Nevertheless, the Agency believes that there are factors in addition to metal concentrations in leachates which justify the T listing. Some of these factors already have been identified, namely that present industry disposal practices have often proven inadequate; the presence of nickel and cyanide, often in high concentrations, two constituents not caught by the (E) characteristic; the nondegradability of the three heavy metals and the high concentrations of cadmium and chromium in actual waste streams.

The quantity of these wastes generated is an additional supporting factor. As indicated above, wastewater treatment sludge from electroplating operations will drastically increase in quantity when the pretreatment standards are implemented in October 1982 and these sludges will contain extremely high cadmium, chromium and nickel concentrations (see p. 10 above). Large amounts of each of these metals are thus available for potential environmental release. The large quantities of these contaminants pose the danger of polluting large areas of ground and surface waters. Contamination could also occur

for long periods of time, since large amounts of pollutants are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or used up due to the large quantities of pollutant available. All of these considerations increase the possibility of exposure to the harmful constituents in the wastes, and in the Agency's view, support a T listing.

#### Health Effects Associated with Hazardous Waste Constituents

The toxicity of cadmium, chromium, nickel and cyanide has been well documented. Capsule descriptions on the adverse health and environmental effects are summarized below; more detail on the adverse effects of cadmium, chromium, nickel, and cyanide can be found in Appendix A.

The Carcinogenicity of various hexavalent chromium compounds in humans is well documented<sup>(15)</sup>, and EPA's CAG has determined that there is substantial evidence that hexavalent chromium compounds are carcinogenic to man. In one study rats showed a weak carcinogenic response to trivalent chromium compounds. Oral administration of trivalent chromium results in little chromium absorption, the degree absorption is slightly higher following administration of hexavalent compounds. Chronic - toxicity problems associated with chromium include damage to liver, kidney, skin, respiratory passages and lungs. Allergic dermatitis can result from exposure to both tri- and hexavalent chromium.

No data for chronic toxicity trivalent chromium for freshwater fish or algae are available. The chronic toxicity value for the freshwater invertebrate Daphia magna, based on a single study, is reported as 445 mg/l (CrIII) and 10 mg/l (CrVI). Chronic embryo-larval tests on six species of freshwater fish exposed to CrVI resulted in values ranging from 37 to 72 mg/l.(15)

Cadmium shows both acute, and chronic toxic effects in humans. The LD<sub>50</sub> (oral, rat) is 72 mg/kg. Excessive intake leads to kidney damage. Cadmium and its compounds have also been reported to produce oncogenic and teratogenic effects. Aquatic toxicity has been observed at sub-ppb levels.

Nickel has been found to bring about a carcinogenic response upon injection in a number of animal studies. Nickel has also been demonstrated to present adverse effects in a three generation study with rats at a level of 5 mg/l (5 ppm) in drinking water. In each of the generations, increased number of runts and enhanced neonatal mortality were seen. Chronic exposure to nickel has also resulted in injury to both the upper and lower respiratory tract in man.

Ferrocyanides exhibit low toxicity, but release cyanide ions and toxic hydrogen cyanide gas upon exposure to sunlight. Cyanide compounds can adversely affect a wide variety of organisms. For example, cyanide in its most toxic form can be fatal to humans in a few minutes at a concentration of 300 ppm. Cyanide is also lethal to freshwater fish at concen-

trations as low as about 50 mg/l and has been shown to adversely affect invertebrates and fishes to concentrations of about 10 mg/l. The hazards associated with exposure to chromium, cadmium, nickel and cyanide have been recognized by other regulatory programs. Chromium, cadmium, nickel and cyanide are listed as priority pollutants in accordance with §307(a) of the Clean Water Act. Under §6 of the Occupational Safety and Health Act of 1970, a final standard for chromium has been promulgated in 29 CFR 1910.1000; permissible exposure limits have also been established for KCN and NaCN. The U.S. Public Health Service established a drinking water standard of 0.2 mg CN/l as an acceptable level for water supplies. In addition, final or proposed regulations for the State of Maine, Massachusetts, Vermont, Maryland, Minnesota, New Mexico, Oklahoma, and California define chromium, cadmium, nickel, and cyanide containing compounds as hazardous wastes or components thereof.(11)

## References

1. U.S. EPA Economic analysis of pretreatment standards for existing sources of the electroplating point source category. EPA No. 440/2-79-031. NTIS PB No. 135 262. August, 1979.
2. U.S. EPA. Assessment of industrial hazardous waste practices, Electroplating and metal finishing industries - job shops, EPA No. 68-01-2664. NTIS PB No. 264 349. September, 1976.
3. Not used in text.
4. American Electroplating Society. Interim Phase I Report: Electroplating wastewater sludge characterization. August 24, 1979; revised September 12, 1979.
5. U.S. EPA. Development document for existing source pretreatment standards for the electroplating point source category. EPA No. 440/1-78/085. February, 1978.
6. U.S. EPA. Composite of State Files. Special wastes disposal applications. Result of leachate tests on cyanide containing wastes from Illinois, Iowa, Kansas and Pennsylvania. 1976-1979.
7. Metal Finishing Guidebook and Directory. V.77, No. 13. Metals and Plastics Publications, Inc., Hackensack, New Jersey/ January, 1979.
8. U.S. EPA. Effluent Guidelines On-going BAT Study.
9. U.S. EPA. Alesii, B.A. and W.A. Fuller. The mobility of three cyanide forms in soil. pp. 213-223. In: Residual management by land disposal. W.H. Fuller, ed., U.S. EPA, Cincinnati, Ohio. NTIS PB No. 256 768. 1976.
10. U.S. EPA. The prevalence of subsurface migration of hazardous chemical substances at selected industrial waste land disposal sites. EPA No. 530/SW-634. U.S. EPA, Washington, D.C. 1977.
11. U.S. EPA. State Regulations Files. January, 1980.
12. U.S. EPA. Cyanides: Ambient water quality criteria. NTIS PB No. 296 792. 1979.

13. U.S. EPA. Open File of Hazardous Waste Incidents.
14. U.S. EPA. Development document for effluent limitations and guidelines and standards for metal finishing point source category. EPA No. 440-1-80-091-A. June, 1980.
15. U.S. EPA. Ambient water quality criteria for chromium. EPA No. 440/5-80-035. October 1980.
16. U.S. EPA. Review of the environmental effects of pollutants; III. Chromium. ORNL/EIS-80; EPA No. 600/1-78-023. May, 1980.
17. Carline, R.L., ed. Transition metal chemistry, V.I. Marcel Dekker, New York. 1965.
18. Latimer, W.M., and J.H. Hildebrand. Reference book of inorganic chemistry. MacMillan, New York. 1940.
19. Griffin, R.A., A.K. Au, and R.R. Frost. Effects of pH on adsorption of chromium from landfill leachate by clay minerals. J. Environ. Sci. Health A12(8): 431-449. 1977.
20. Bartlett, R.J., and J.M. Kimble. Behavior of chromium in soils: I Trivalent forms. J. Environ. Qual. 5:379-383. 1976.
21. National Academy of Sciences. Medical and biological effects of environmental pollutants; chromium. Washington, D.C. 1974.
22. U.S. EPA. Application of sewage sludge to cropland; appraisal of potential hazards of the heavy metals to plants and animals. EPA No. 430/9-76-013. NTIS PB No. 264 015. November, 1976.
23. Bartlett, R.J., and J.M. Kimble. Behavior of chromium in soils:II. Hexavalent forms. J. Environ. Qual. 5:383-386. 1976.
24. Comments from Reynolds Aluminum. July 18, 1980.
25. Memorandum from Mike Keller and Gay Contos to Matt Straus. Subject: Chemical conversion coating process, dated September 17, 1980.

Attachment I

Damage Incidents Resulting From the Mismanagement  
of Electroplating Wastes(13)

Columbia County, Pennsylvania (1965) - Unlined lagoons caused contamination of a number of private wells in the area. The lagoons contained plating wastes and were leaking such pollutants as cyanide, copper, nickel, alkylbenzenesulfonate and phosphate.

Illinois - At a farm site in Illinois used for the dumping of highly toxic industrial wastes (mostly from metal finishing operations), three cows died as a result of cyanide poisoning and extensive danger occurred to wildlife, aquatic biota and vegetation. Additionally, crops cannot be safely grown in the area again.

Bronson, Michigan (1939) - Since 1939, electroplating industries in Bronson, Michigan have experienced difficulty in disposing of their electroplating wastes. Originally, the wastes were discharged into the city's sewer system which was subsequently emptied into a creek. Contamination of this water resulted in the death of fish and cattle below Bronson from cyanide poisoning. All the plating wastes of the company were subsequently discharged to ponds.

Lawrenceburg, Tennessee - Between 1962 and 1972 in Lawrenceburg, Tennessee, an industry dumped up to 5,000 gallons of untreated

metal plating waste daily into trenches near the city dump: Significant concentrations of hexavalent chromium and traces of cyanide were measured in an adjacent stream by several local residents as a drinking water supply.

South Farmingdale, New York - An aircraft plant, operating in South Farmingdale on Long Island during World War II, generated large quantities of electroplating wastes containing chromium, cadmium and other metals. It has been estimated that between 200,000 to 300,000 gallons per day of these wastes were discharged into unlined disposal basins throughout the 1940's. A treatment unit for chromium was constructed in 1949, but discharge of cadmium and the other metals continued. The local groundwater flows in three unconsolidated aquifers resting on crystalline bedrock. The uppermost aquifer consists of beds and lenses of fine-to-coarse sand and gravel and extends to within 15 feet of the land surface. Groundwater contamination by chromium was first noted in 1942 by the Nassau County Department of Health. Extensive studies in 1962 indicated that a huge plume of contaminated groundwater had been formed, measuring up to 4,300 feet long, 1,000 feet wide and extending from the surface of the water table to depths of 50 to 70 feet below the land surface. Maximum concentrations of both chromium and cadmium were about 10 mg/l in 1962. (Chromium had been measured as high as 40 mg/l in 1949.) This huge contaminated plume cannot be removed or detoxified without massive efforts and will take many

more years of natural attenuation and dilution before it becomes useable again. Meanwhile, the plume is still slowly moving, threatening a nearby creek and other wells in the area.

Kent County, Michigan - An aquifer used for a municipal waste supply was contaminated by chromium leachate from a sand and gravel pit used as a landfill. The landfill had been taken from a former dumping ground for electroplating wastes. The fill material was removed to ameliorate the pollution problem.

Allegan County, Michigan (1947) - Wells produced yellow water which contained high levels of chromium. About three years before any contamination appeared, a metal-plating company began discharging chrome-plating wastes into an infiltration pit and the surrounding overflow area. Discharge of plating wastes resulted in the contamination of the glacial-drift aquifer. Health Department personnel estimated it would be about six years before the aquifer in the vicinity of the wells would be free of chromate. All private wells in the village of Douglas were condemned.

Riverside County, California (1956) - Chrome plating wastes were discharged on the ground and into a cesspool. Samples from four wells contained concentrations of hexavalent chromium of as much as 3 mg/l and 18 others contained trace amounts. The National Interim Primary Drinking Water Standard for total chromium is 0.05 mg/l.

Attachment II

Solubility and Environmental Mobility Characteristics  
of Chromium Compounds

The tripositive state is the most stable form of chromium. In this state chromium forms strong complexes (coordination compounds) with a great variety of ligands such as water, ammonia, urea, halides, sulfates, amines and organic acids.(16,17) Thousands of such compounds exist. This complex formation underlies the tanning reactions of chromium, and is responsible for the strong binding of trivalent chromium by soil elements, particularly clays.

At pH values greater than about 6, trivalent chromium forms high molecular weight, insoluble, "polynuclear" complexes of  $\text{Cr}(\text{OH})_3$  which ultimately precipitate as  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . This process is favored by heat, increased chromium concentration, salinity and time.(16) These chromium hydroxy complexes, formed during alkaline precipitation treatment of Cr-bearing wastes, are very stable, and relatively unreactive, because the water molecules are very tightly bound. In this form, Cr is therefore, resistant to oxidation. Three acid or base catalyzed reactions are responsible for the solubilization of chromium hydroxide:

<u>Reaction</u>	<u>Keq.(18)</u>	<u>Resulting Calculated CrIII Concentration mg/l</u>		
		<u>pH5</u>	<u>pH6</u>	<u>pH7</u>
1. $\text{Cr(OH)}_3 + 2\text{H}^+ \rightleftharpoons \text{CrOH}^{++} + 2\text{H}_2\text{O}$	$10^8$	520	5.2	0.052
2. $\text{Cr(OH)}_3 \rightleftharpoons \text{Cr}^{+3} + 3\text{OH}^-$	$6.7 \times 10^{-31}$	35	0.035	1*
3. $\text{Cr(OH)}_3 \rightleftharpoons \text{H}^+ + \text{CrO}_2^- + \text{H}_2\text{O}$	$9 \times 10^{-17}$	1	1	1

\*i=<0.001 mg/l

It is apparent from these figures that, in theory, trivalent chromium could leach from sludges to some extent. Such solubilized chromium, however, is unlikely to contaminate aquifers. It is complexed with soil materials, and tenaciously held.(16,17) Little soluble chromium is found in soils.(10,12) If soluble trivalent chromium is added to soils it rapidly disappears from solution and is transformed into a form that is not extracted by ammonium acetate or complexing agents.(12,13) However, it is extractable by very strong acids, indicating the formation of insoluble hydroxides.(19,20) Thus: above pH5, chromium(III) is immobile because of precipitation; below pH4, chromium (III) is immobile because it is strongly absorbed by soil elements; between pH4 and 5 the combination of absorption and precipitation should render trivalent chromium quite immobile.(19,20)

In contrast, hexavalent chromium compounds are quite soluble, and hexavalent chromium is not as strongly bound to

soils.(19,21) Hexavalent chromium remains as such in a soluble form in soil for a short time, and is eventually reduced by reducing agents if present.(22,23) As compared with the trivalent form, hexavalent chromium is less strongly adsorbed and more readily leached from soils(19) and thus, is expected to have mobility in soil materials.(19)

Response to Comments - Wastewater Treatment Sludges from  
Electroplating Operations

A number of comments have been received with respect to waste F006 (Wastewater treatment sludges from electroplating operations).

1. One commenter pointed out that EPA's original proposal to list "electroplating wastewater treatment sludges" (43 FR 58958), and the background document which accompanied this proposal, did not specifically propose to include anodizing operations and chemical conversion coating operations within the electroplating wastewater treatment sludge designation. Therefore, the commenter argues that the May 19, 1980 listing expanded what was originally included in the proposed listing description without allowing for adequate public comment or clearly stating that this designation has been expanded.

The Agency disagrees with the commenter. Although the term "electroplating" was not specifically defined either by the listing or appropriate background document, the term was defined by the Agency under regulations promulgated by the Effluent Guidelines Division (EGD). It has been Agency policy to use the same definitions for the same terms throughout the Agency to avoid confusion among the regulated community. Only when the Agency intentionally defines terms differently would

the Agency believe it has an obligation to inquire whether a listing description --in this case "electroplating wastewater treatment sludges"-- encompassed the same processes as those defined under the EGD regulatory program.

2. A number of commenters objected to the inclusion of the sulfuric acid anodizing process in the general category of electroplating operations, and the subsequent inclusion of these process sludges as hazardous wastes in §261.31. The commenters first point out that the anodizing of aluminum is not an electroplating operation. Rather, it is an operation which etches and oxidizes the aluminum as compared to the plating of a different metal which occurs in electroplating. Secondly, the commenters indicate that the two major processes used in aluminum anodizing, chromic acid process and sulfuric acid process, are entirely different. The chromic acid process uses chromium rich solutions, so that chromium would be expected in the waste, while the sulfuric acid process does not use chromium, cadmium, nickel or cyanide-rich solutions. Therefore, the commenters argue that wastewater treatment sludges from the sulfuric acid anodizing process would not be expected to contain significant concentrations of these contaminants, and thus recommend that wastes generated from the sulfuric acid anodizing

process be excluded in the general category of electroplating operations and removed from the hazardous waste list.

In reviewing the various electroplating processes, including the two primary processes used in aluminum anodizing, the Agency generally agrees with the commenters and has modified the listing to exclude wastewater treatment sludges generated from the sulfuric acid anodizing processes. However, the Agency also believes that it may not be accurate to portray the wastes from either process (i.e., the chromic acid and sulfuric acid processes) as non-hazardous in all cases solely on the basis of the anodizing solution. To improve the corrosion resistance of anodic coatings on aluminum, the anodized surface is immersed into slightly acidified hot water. The sealing process converts the amorphous anhydrous aluminum oxide to the crystalline monohydrate ( $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ). For sulfuric oxide anodized parts, 5-10% by weight sodium dichromate can be added (the use of sodium dichromate as a sealer for uncolored sulfuric anodizing is a recognized non-proprietary industrial process\*). Consequently, the amount of chromium in sulfuric acid anodizing sludges may be significant. Additionally, unsealed anodic coatings on aluminum are

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\*Chuck Bent, Reynolds Aluminum, August 27, 1980. Personal communication.

colored by immersion in a solution of organic or inorganic dyes. After rinsing, the sealing of the dye is accomplished by immersion in a hot solution of nickel or cobalt acetate. Therefore, the amount of nickel in these sludges may also be significant. However, the available information indicates that both chromium and nickel are used infrequently as sealants in this process (i.e., the large majority of the industry uses a plain hot water bath in the sealing process). Therefore, the Agency will only use the characteristics (principally the EP toxicity characteristic)\* to determine whether these wastes are hazardous at this time. If after further study, however, the Agency finds that both sodium dichromate and nickel acetate are commonly used in the sulfuric acid anodizing process and that these toxic contaminants end up in the waste in significant concentrations, the Agency will consider bringing these sludges back into the hazardous waste system by listing.

3. One commenter objected to the inclusion of wastes from chemical conversion coating operations as hazardous wastes, especially with respect to coating operations of aluminum. The commenter argues that the listing background document contains a rather unspecified scenario

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\*By relying on the characteristics, those sludges which contain significant concentrations of nickel would not be brought into the hazardous waste system.

on the potential adverse effects of cadmium, chromium, nickel and cyanide and that this scenario is clearly not appropriate for sludges from chemical conversion coating operations. The commenter also points out that neither cadmium, nickel or cyanide are present in wastes from the chemical conversion coating of aluminum in significant concentrations (the EP was conducted on two chemical conversion coating waste treatment plant sludges, and showed low concentrations of these metals). With respect to chromium, the commenter believes that the concentrations of this contaminant in the EP extract from the two sludge samples (Sample A - 3.24 mg/l Cr and Sample B - 0.16 mg/l Cr) provides no basis for listing these wastes as hazardous. The commenter therefore recommends that the listing F006 (wastewater treatment sludges from electroplating operations) be revised to exclude wastes from the chemical conversion coating of aluminum.

The Agency disagrees with the commenter. Although the listing background document does not provide a specific discussion on chemical conversion coating operations and includes only limited data on the composition and concentrations of the toxic constituents in these sludges, data contained in the references to the background document fully support the listing of sludges from chemical conversion coating operations. For example,

in the Agency's Development Document for Existing Source Pretreatment Standards for the Electroplating Point Source Category,<sup>(5)</sup> effluent streams from forty-six coatings plants were sampled and analyzed for a number of compounds including cyanide and chromium. The results of this sampling effort are presented below:

Composition of Raw Waste Streams  
from Coatings Process (mg/l)

<u>Compound</u>	<u>Concentration</u>
CR (Total)	.19 - 79.2
Cyanide	.005 - 126.0

As is indicated, these toxic compounds are present in the raw wastewater, thus can be expected to be found in the treatment sludges, at much higher concentrations, after implementation of the electroplating pretreatment standards. The Agency believes that these sludges are no different (i.e, would contain toxic metals and complex cyanides in significant concentrations) than other electroplating sludges which have been shown to leach. Additionally, it should be pointed out that conversion coating processes are usually associated with electroplating operations and, thus, wastes from conversion

coating operations are most likely to be combined with those of other metal finishing operations of similar waste characteristics and treated in a single treatment plant. Therefore, the Agency will continue to include the general category of chemical conversion coating operations in the electroplating category, so that these process sludges will continue to be listed as hazardous wastes. However, the listing background document will be revised to include a more detailed discussion of chemical conversion coating operations.

With respect to the specific category of chemical conversion coating of aluminum, the Agency also has decided to continue to include these sludges as part of the hazardous waste listing. This decision is based, after careful review of the process, on the frequent use of chromate compounds in the various conversion coating operations on aluminum. Thus, sodium chromate or potassium dichromate is used in common oxide-conversion coating solutions, potassium dichromate is used in phosphate-conversion coating solutions, and sodium dichromate is used in chromate-conversion coating solutions.<sup>(25)</sup> Although limited analytical data is available, the Agency believes that the chromium used in the process will end up in the raw wastewater and subsequently precipitate out into the treatment sludges. In data submitted by one commenter, the level of chromium found

in the EP extract from one sludge sample was 3.24 mg/l (approximately 65 times the NIPDWS), a level considered significant by the Agency.\*<sup>(24)</sup> Additionally, cyanides are known to be used in the coloring of anodized aluminum.<sup>(5)</sup> Therefore, the Agency will continue to list sludges from the chemical conversion coating of aluminum. However, since this waste is not expected to contain significant concentrations of cadmium and nickel, the Agency has decided to list these sludges separately for the presence of chromium and cyanide as the only constituents of concern.

4. Several commenters felt that the listing "Wastewater treatment sludges from electroplating operations" was overly broad. More specifically, the commenters indicate that the listing will require industry to manage the following electroplating baths, sludges and solutions as hazardous wastes: (1) tin plating on carbon steel, (2) zinc plating (segregated basis) on carbon steel, (3) aluminum or zinc-aluminum plating on carbon steel (4) all cleaning and stripping associated with tin, zinc and aluminum plating on carbon steel and (5) chemical etching and milling of aluminums. Commenters argue that these

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\*Data was also submitted by the commenter which indicates that the level of chromium found in the EP extract (0.16) can be insignificant, However, this one data point is insufficient to remove all sludges from this process from the hazardous waste listing.

processes do not use chromium, cadmium, nickel and cyanide solutions, and thus that these compounds are not expected to be present in the sludges, and also that no data was presented in the listing background document to support the inclusion of these processes in the listing. Therefore, they recommend that the Agency revise the listing to exclude the plating of tin, zinc (segregated basis) and aluminum on carbon steel and chemical etching and milling of aluminum from this listing.

In reviewing the various electroplating processes, the Agency agrees with the commenters that the above electroplating processes would not generate a sludge which would contain significant concentrations of chromium, cadmium, nickel and cyanide. We have consequently modified the listing to exclude wastewater treatment sludges generated from: (1) tin plating on carbon steel, (2) zinc plating (segregated basis) on carbon steel, (3) aluminum or zinc-aluminum plating on carbon steel, (4) all cleaning/stripping associated with tin and aluminum on carbon steel, and (5) chemical etching and milling of aluminum from the hazardous waste listing.

## Listing Background Document

### SPENT WASTE CYANIDE SOLUTIONS AND SLUDGES

#### 1. LISTING

The listed wastes are those waste streams, from several industry segments which specifically contain cyanide salts or complexed cyanide compounds. These listing descriptions have been modified to make it clear that only those processes which use cyanide salts or complexed cyanide compounds are covered by the listing. These wastes are generically listed as follows:

#### Cyanide Salts

##### Electroplating

Spent cyanide plating bath solutions (except for precious metals electroplating spent cyanide plating bath solutions)(R,T)\*

Plating bath sludges from the bottom of plating baths where cyanides are used in the process (except for precious metals electroplating plating bath sludges)(R,T)

Spent stripping and cleaning bath solutions where cyanides are used in the process (except for precious metals electroplating spent stripping and cleaning bath solutions)(R,T)

##### Metal Heat Treating

Quenching bath sludge from oil baths where cyanides are used in the process (except for precious metals heat-treating quenching bath sludge)(R,T)

Spent cyanide solutions from salt bath pot cleaning (except for precious metals heat-treating spent solutions from salt bath pot cleaning)(R,T)

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\*Spent plating bath solutions and plating bath sludge from the bottom of plating baths also contain complexed cyanides, but are more significant as sources of cyanide salts.

Mineral Metals Recovery

Spent cyanide bath solutions (R,T)

Complexed Cyanides\*

Metal Heat Treating

Quenching wastewater treatment sludges where cyanides are used in the process (except for precious metals heat-treating quenching wastewater treatment sludges)(T)

Mineral Metals Recovery

Cyanidation\*\* wastewater treatment tailing pond sediment (T)

II. SUMMARY OF BASIS FOR LISTING

A number of different industry categories located nationwide dispose of spent or waste cyanide solutions and sludges, the most prevalent being electroplating, metal heat treating and mineral metals recovery operations. Cyanide is present in these wastes in the form of either (1) alkali-metallic or alkaline earth cyanide salts such as sodium, potassium, and calcium cyanide or (2) as heavy metal cyanides, ferro- and ferricyanides, and ferric ammonium ferrocyanide (iron blue) referred to as complexed cyanides.(1)

The Administrator has determined that wastes from these processes may be solid wastes, and as solid wastes may pose a substantial present or potential hazard to human health and

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\*In response to comments, two of the listings ("Flotation tailings from selective flotation from mineral metals recovery operations" and "Dewatered air pollution control scrubber sludges from coke ovens and blast furnaces") which were promulgated on May 19, 1980 (45 FR 33123) have been deleted from the hazardous waste list. See Response to Comments in back of the background document for details.

\*\*Cyanidation as described in this background document is meant to include the recovery of gold via a caustic cyanide leach. Cyanidation can also be used to recover silver; however, domestically little if any silver is recovered by cyanidation except when silver is recovered as a by-product from gold recovery operations.(1)

the environment when improperly transported, treated, stored, disposed of or otherwise managed, therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. Each of the wastes exhibits either reactive or toxic properties or both due to their cyanide content.
2. These wastes generally contain high concentrations of cyanide. Additionally, land disposal of cyanide wastes is widespread throughout the United States with 769 kkg of cyanide (CN<sup>-</sup>) contained in these wastes annually. Thus, the high cyanide concentration levels and the large annual generation rate, increases the likelihood of exposure and possibility of substantial hazard.
3. Cyanides can migrate from the waste to adversely affect human health and the environment by the following pathways, all of which have occurred in actual management practice:
  - (a) generation of cyanide gas resulting from the reactive nature of cyanide salts when mixed with acid wastes;
  - (b) contamination of soil and surface waters in the vicinity of inadequate waste disposal resulting in destruction of livestock, wildlife, stream-dwelling organisms, and local vegetation; and
  - (c) contamination of private wells and community drinking water supplies in the vicinity of inadequate waste disposal.

### III. SOURCES OF CYANIDE WASTE AND TYPICAL DISPOSAL PRACTICES

#### A. Overall Description of Industry Sources

Waste cyanide solutions and sludges containing both cyanide salts and complexed cyanides are generated by a number of different industries including electroplating, metal heat treating and mineral metals recovery operations. Approximately

20,000 facilities in the United States use one or more electroplating or heat treating processes in manufacture of primary metals, fabricated metals, machinery, and electronics equipment.(6) An additional 5 facilities use cyanide in the process of recovering precious metals, particularly gold and silver. (Complexed cyanide waste solutions or sludges containing only complexed cyanide are generated by a number of other industrial processes, principally iron blue manufacturing.\*)

Table 1 lists the equivalent cyanide (CN<sup>-</sup>) consumed annually by each of these processes including the specific types of cyanide salts and complexed cyanides used. Table 2 indicates the number of facilities and types of waste associated with these different sources. Industrial processes which generate these waste cyanide solutions and sludges are further described below.

B. Waste Generation, Waste Stream Description and Waste Management Practices

The major processes which generate cyanide salt-containing waste include (1) electroplating using cyanide plating baths or cyanide stripping or cleaning baths, (2) metal heat treating using cyanide quenching baths, and (3) mineral metals recovery using cyanide plating baths. Complexed cyanide wastes (primarily ferro and ferricyanides) are generated from

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\*Iron blue manufacturing is discussed in the chromium pigments background document and thus is not presented here.

Table 1

Equivalent Cyanide (CN<sup>-</sup>) Consumed Annually By  
Process and By Specific Type (Salts or Complexed)<sup>(4)</sup>

<u>Cyanide Salts</u>	<u>Electro-</u> <u>plating</u>	<u>Heat</u> <u>Treating</u>	<u>Mineral</u> <u>and</u> <u>Metals</u> <u>Recovery</u>
NaCN	10,292	1,428	unknown <sup>(a)</sup>
KCN	72	65	--
CaCN <sub>2</sub>	-	-	--
<u>Complexed Cyanides</u>			
Heavy Metal	2,346	-	--
Ferrocyanides	-	65	--
Ferricyanides	-	-	--
TOTAL	12,710	1,558	--

(a) MRI (1976) has estimated that about 650 kkg of NaCN is used for precious metal cyanidation;<sup>(1)</sup> however, one of the cyanidation precious metal operations uses a copper ore and, thus, an unknown fraction of this total is not used primarily for precious metals recovery.

Table 2  
CYANIDE WASTE SOURCES

Source	Number of Facilities	Types of Wastes(s)
Electroplating	13, 000(a)	Cyanide salts and complexed cyanides (Solution and sludge)
Minerals and Metals Recovery	5(1)	Cyanide salts and complexed ferro and ferricyanide (solutions and sludges in tailing ponds)
Metal Heat Treatment	7,000(a)	Sodium and potassium cyanide (solution and sludge)

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(a)Based on Oct. 1979 Effluent Guidelines document estimates. (U.S. Environmental Protection Agency. Oct., 1979. Draft Development for Effluent Limitations Guidelines, New Source Performance Standards and Pretreatment Standards for the Photographic Processing Point Source Category. Washington, D.C.).

(1) treatment of electroplating wastewater (2) treatment of quenching process wastewater from the metal heat treating industry and (3) treatment of cyanidation wastewater from mineral metals recovery operations.

1. Electroplating

a. Generation of Spent Plating, Stripping and Cleaning Bath Solutions

Electroplating, as defined in this document, includes both common and precious metal electroplating, anodizing, chemical conversion coating (i.e., coloring, chromating, phosphating and immersion plating), chemical etching and milling, electroless plating, and printed circuit board manufacturing. The primary purpose of electroplating operations is to apply a surface coating, typically by electrode decomposition, to provide protection against corrosion, to increase wear or erosion resistance, to restore worn parts to their original dimensions, or for decoration.<sup>(7)</sup> The operation itself involves immersing the article to be coated/plated into a bath consisting of acids, bases, salts, etc. A plating line consists of a series of unit operations conducted in a sequence in which one or more coatings are applied or a basis material is removed. (For a more detailed discussion of the electroplating process see the Development Document for Existing Source Pretreatment Standards for the Electroplating Point Source Category, August 1979).<sup>(7)</sup>

Figure I-1 in Appendix I illustrates a standard electroplating process. Cyanides may be used to make-up the various plating/coating solutions and stripping and cleaning bath solutions.<sup>(7)</sup> For example, the electrolytic baths used in both chromium and precious metal electroplating typically consist of cyanide salts of sodium, potassium, cadmium, zinc, copper, silver, and gold.<sup>(1)</sup> After extended use, plating baths become deficient in the specific ion being plated/coated, leaving cyanides in solution either as simple ions or in complexes. After extended use of stripping and cleaning solutions, metals begin to accumulate so that further removal of metal coatings on articles becomes difficult. At that point these solutions are either processed for metal recovery (this is particularly true of precious metal plating operations) or discarded. Untreated spent plating, stripping and cleaning bath solutions, when discarded, represent the major sources of cyanide salt containing wastes generated in electroplating operations\* (and a minor source of complexed cyanides).

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\*Another major source of cyanide salt waste is the rinse water contaminated by the solution remaining on the article that has been plated, stripped, or cleaned. This rinsewater is either treated and present in wastewater treatment sludge, in which case it is part of a listed waste, or discharged directly to a POTW. Rinsewater which is mixed with domestic sewage that passes through a sewer system before it reaches a POTW for treatment is excluded from subtitle C regulation under §261.4(a)(1). The Agency is in the process of developing pre-treatment standards for the electroplating industry.

b. Management of Spent Plating, Stripping and Cleaning Bath Solutions, and Generation of Treatment Sludges

Spent plating, stripping and cleaning bath solutions and rinse waters containing cyanide compounds are chemically treated, primarily with hypochlorite or chlorine, to convert cyanide compounds to carbon dioxide, metal salts, nitrogen, and water.(7)

Complexed cyanides that are present in hypochlorite-treated bath solutions and rinse waters are precipitated as part of the sludge during any additional wastewater treatment (see Figure I-2 in Appendix I). Even though the cyanide is treated, a certain percentage of the complexed cyanide is not destroyed and thus may be present in the sludges.(1,8) These sludges are typically disposed of in a sanitary landfill.(1,8)

c. Plating bath sludge from the bottom of cleaning baths

Additionally, cyanide plating solutions that have been restored several times often leave a sludge in the bottom of the bath which must be cleaned out when spent solutions are discarded. These sludges often contain cyanide salts and complexed cyanides when cyanide solutions are used in the process and typically are placed in drums for chemical landfill disposal.(1)

Available plant information indicates that nearly all of the cyanide-containing materials discharged to the environment are treated, although it is possible that some small plating shops may either discharge directly to municipal sewer systems or landfill spent solutions.(1)\*

## 2. Metal Heat Treatment

### a. Generation of Cyanide-Containing Quenching Bath Sludge and Spent Solutions from Salt Bath Pot Cleaning

Case hardening by carburizing adds carbon to the surface of steel.(7) Liquid carburizing uses cyanides as the source of carbon. Liquid carburizing is accomplished by submerging the metal in a molten salt bath containing sodium cyanide (6-23%). Figure I-3 in Appendix I illustrates the liquid carburizing process. Sodium cyanide is also used in the case hardening of steel using either the liquid nitriding or carbonitriding processes.

Cyanide salt-containing wastes from this process generally arise from two sources: (1) quenching sludge and (2) pot cleanout. In the quenching process, oil is used as the quenching media. The sodium cyanide adhering to the case hardened steel during oil quenching is not soluble and

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\*However, since 60 to 80 percent of these small plating shops have shifted to non-cyanide baths (such as zinc), the quantity of untreated cyanide waste landfilled from electroplating operations is getting smaller.(1)

settles to the bottom of the quenching tank as a sludge. Another source of cyanide waste (although generated in less volume than the quenching sludge) results from cleaning out salt bath pots.

b. Generation of Quenching Wastewater Treatment Sludge

Where process wastewaters containing cyanides are chemically treated, sludges from these operations are typically disposed of in landfills.(10) During waste treatment some of the untreated cyanide may complex with heavy metals and precipitate in the sludge.(7)

3. Mineral and Metals Recovery

Cyanides are used extensively in the extraction and beneficiation of gold and silver from ore.

a. Generation and Management of Cyanidation Wastewater Tailings Pond Sediment

Use of cyanide (cyanidation) in the recovery of gold and, to a lesser extent, silver, varies in process complexity depending on the ore matrix. Generally, the ore is pulverized to expose gold and silver deposits prior to leaching by caustic cyanide solutions.(1) The gold or silver-laden caustic cyanide solution is then electrolyzed, and the gold or silver is deposited on stainless steel wool cathodes (see Figure I-4 in Appendix I). The cyanide bath is then chemically treated with hypochlorite or chlorine to

destroy cyanide salts and complexes. The resulting wastewater tailings pond sediment is a listed waste. Ferrocyanide and ferricyanide complexes formed in tailings pond sediment are periodically dredged and disposed of in landfills.(1)

b. Generation of Spent Cyanide Bath Solutions(1)

This waste stream also arises from the cyanidation process described above. Some minerals and metals recovery plants, however, instead of chemically treating spent cyanide bath solutions, discharge the waste directly to tailing ponds where oxidation and sunlight are relied upon to convert cyanide salts to complex cyanides which precipitate into the pond sediment. In this case, the listed waste stream is the spent cyanide bath solution.

c. Waste Characteristics and Quantities

Waste cyanide solutions and sludges are generated nationwide with most disposal occurring in EPA Regions I through IV and in Region IX.(10) The quantity and types of wastes that result from any of these processes are variable and depend upon operation conditions at each facility, but significant cyanide concentrations in all of these waste streams are anticipated. Nearly all cyanide processes include some form of chemical treatment which destroys most of the cyanide prior to precipitation of solids and heavy metals. Of the total 14,260 kkg equivalent cyanide consumed annually,

12,710 kkg is used by the electroplating industry.<sup>(4)</sup> A large percentage of that is either oxidized by electrolysis in the plating bath, destroyed during alkaline chlorination or ozonation prior to wastewater discharge.<sup>(1)</sup> This means that approximately 127 kkg of equivalent cyanide (CN<sup>-</sup>) (probably in the salt form) is disposed of annually on land by this industry. Of the remaining 1,557 kkg (from the total of 14,260 kkg) equivalent cyanide (CN<sup>-</sup>) consumed annually, about 41 percent (769 kkg - 127 kkg = 642 kkg) is disposed of on land as solutions or sludges.<sup>(4)</sup> The balance is either recovered or chemically destroyed by alkaline chlorination, electrolysis, or ozonation. Sixty-seven percent of this 642 kkg of CN<sup>-</sup> disposed of (by industries other than electroplating) is in complexed cyanide form.

Table 3 lists the types of cyanide wastes generated, the range of quantity disposed of in solid waste streams by an individual facility, and the total quantity of waste for each of the contributing sources of manufacturing processes. These quantities are considered significant in light of cyanide's migratory potential (see p. 21-24) and high toxicity. The fact that disposal occurs nationwide is also significant, since the wastes are exposed to many differing environmental conditions and management situations, increasing the possibility of mismanagement.

Cyanide is expected to be present in most of these waste streams in high concentrations. Table 3A contains cyanide salt and complexed cyanide concentration data from listed electroplating and metal heat treating wastes. Concentrations range from 38 ppm to 92,300 ppm, with most concentrations exceeding 1,000 ppm. In light of the health dangers associated with cyanide (see pp. 27-28 below), these concentrations are deemed to be of regulatory concern.

The Agency presently lacks concentration data on the cyanidation wastes generated by the mineral metals recovery industry, although concentrations are believed to be high based on the large quantity of cyanides disposed of annually. (See Table 3)

D. Typical Disposal Practices

In general, waste management of cyanide solutions and sludges relies primarily on disposal in municipal, chemical, or company-owned landfills.<sup>(1)</sup>

Facilities using only one process, sometimes find it more cost effective to landfill spent cyanide salt solutions (without any chemical treatment) along with cyanide sludges.<sup>(1)</sup> Of course, as described above, most spent solutions are managed initially in holding ponds, which are treatment facilities under RCRA.

Spent cyanide solutions and sludges from electroplating operations are generally treated by alkaline chlorination prior to discharge into municipal sewer systems or landfill disposal. Data characterizing the disposal practices in some states indicate, however, that some small plating shops dispose of spent plating solutions and sludges which still contain untreated cyanide in landfills.<sup>(1)</sup>

**Table 3**  
**Waste Characteristics (1,2,7,10)**

<u>Source</u>	<u>Type of Waste</u>	<u>Annual Waste Quantity/Facility kkg</u>	<u>Cyanide (CN<sup>-</sup>) Quantity Used/ Facility (kkg)</u>	<u>Total Annual Waste Quantity (kkg)</u>	<u>Cyanide Salts (CN<sup>-</sup>) Disposed Annually (kkg)</u>	<u>Complexed Cyanides (CN) Disposed Annually (kkg)</u>
Electroplating	Spent plating, Stripping and Cleaning bath solutions; plating bath sludge; plating bath and rinse water treatment sludge	25-1,250(a)	--	42,000 (b)		--
Mineral and Metals Recovery	Cyanidation waste- water treatment sludge	--	20-300(d)	--	0	1-10(j)
Metal Heat Treating	Quenching bath sludge and spent bath solution and quenching waste- water treatment sludge	11-51(f)	0.2-1.1(b)	6,125(10)	759(1)	--

<sup>a</sup>Quantities based on the range in number of number of employees per facility 10-500 employees(7)

<sup>b</sup>Total based on estimated 16.8 employees per facility(1); 10,000 facilities(7); and 2.5 kkg/yr-employee (wet basis)(10) (see figure 1)

<sup>c</sup>Total based on estimated 62% of total consumption of 20,500 kkg (CN) and 1% disposal(1)

(continued)

Table 3 (Continued)

<sup>d</sup>Total based on mining capacity: estimated total consumption is 650 kkg.(1)

<sup>e</sup>50% of NaCN equivalent consumption(1)

<sup>f</sup>Range of total annual waste for facilities included in a composite of state waste disposal applications assuming waste density 4kg/gallon(2). Based on total waste disposal estimates average quantity per facility is 3.5 kkg/yr(10).

<sup>g</sup>Total based on estimated 25 employees per facility; 7,000 facilities of which 25% use cyanide(1); 0.14 kkg/yr-employee(10) (See figure 1)

<sup>h</sup>Range of content of waste per facility for facilities included in a composite of state waste disposal applications assuming waste density and kg/gallon(2)

<sup>i</sup>Total based on estimate that 13% of waste are cyanide wastes and 25% of all cyanide waste is destroyed.

<sup>j</sup>Estimate based on raw waste load data from "Development document for interim final and proposed effluent limitations guidelines and new source performance standards for the ore mining and dressing industry point source category." Volume 1.

Table 3A  
Cyanide Wastes (2)  
Concentrations

<u>Industry</u>	<u>Source*</u>	<u>Typed of Waste/Form**</u>	<u>Annual Disposal in Gallons</u>	<u>Cyanide Concentrations ppm</u>
<u>Cyanide Salts</u>				
Metal Heat Treating	Quenching Bath sludge and Spent Solution	Potassium and Sodium Cyanide/Solid**	3,000	92,300
Metal Heat Treating	Quenching Bath sludges	Potassium and Sodium Cyanide/Sludge	13,200	8,530
Electroplating	Spent Cleaning Bath Solution	Sodium Cyanide/Solution	22,500	350,000
Electroplating	Spent Cleaning Bath Solution	Cyanide Salts/Solution	14,000	38
Electroplating	Spent Plating Bath Solution	Sodium Cyanide Solution	6,600	14,547
Electroplating	Plating Bath Sludge	Metal Salts/Sludge	1,000	64
<u>Complexed Cyanides</u>				
Electroplating	Plating Bath Treatment Sludge	Complex Metal Cyanide/Solution	15,600	80
Electroplating	Spent Plating Bath Solution	Complex Metal Cyanide/Solution	6,600	14,329
Electroplating	Spent Plating Bath Solution	Complex Metal Cyanide/Solution	36,000	2,000
Electroplating	Plating Bath Treatment Sludge	Complex Metal Cyanide/Sludge	12,000	1,681
Metal Heat Treating	Quenching Wastewater Treating Sludge	Complex Metal Cyanide Solids***	6,600	26,803

Table 3A  
Cyanide Wastes(2)  
Concentrations  
Continued

<u>Industry</u>	<u>Source*</u>	<u>Type of Waste/Form**</u>	<u>Annual Disposal in Gallons</u>	<u>Cyanide Concentrations ppm</u>
Metal Heat Treating	Quenching Wastewater Treatment Sludge	Complex Metal Cyanides/Sludge	5,500	8,400

\*Source descriptions included in special waste disposal applications were not always the same as those presented in the listing(2). An attempt was made to classify the waste in its approximate category

\*\* These descriptions were taken directly from the special waste disposal applications(2).

\*\*\* Solid cyanide wastes are placed in drums and disposed of. Solid waste quantities are expressed in gallons related to the size of the drum used to containerize waste for disposal.

Mineral and metals recovery wastes from extraction of gold and silver (cyanidation) are disposed of in tailing ponds which may be lined with clay and are sometimes constructed to control run-off and dam seepage.<sup>(1)</sup> The size, construction, and location of tailing ponds and retention of waste solutions in ponds varies from site to site. When wastes are not alkaline chlorinated to destroy cyanide prior to disposal, tailing ponds are used as holding ponds where natural air oxidization and sunlight destroy the cyanide or where the cyanides are complexed with metals in solution and by attachment to gangue materials.<sup>(1)</sup>

This data suggests that cyanide-containing wastes are sometimes managed properly. Many damage incidents involving cyanide-containing wastes (set forth at pp. 25-27 below)\* indicate, however, that waste mismanagement may occur and cause substantial hazard. Furthermore, proper management of wastes capable of causing substantial hazard if mismanaged does not make a waste non-hazardous under the definition of hazardous waste contained in Section 1004(5) of RCRA. In fact, industry management practice described above suggests strongly that industry itself regards these wastes as hazardous and requiring careful management.

#### IV. HAZARDS POSED BY THE WASTES

Cyanide salt-containing wastes exhibit both reactive and toxic properties which make them potentially hazardous to

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\*Additional damage incidents are described in the electroplating waste background document.

human health and the environment. If exposed to mild acid conditions, these wastes can react to generate toxic hydrogen cyanide gas. Cyanide wastes are land disposed and if improperly managed, cyanide can migrate from these wastes as toxic hydrogen cyanide gas or in a soluble form into groundwater or surface water supplies. Adverse health effects on landfill operators and environmental stress to avian and possibly human populations is possible if hydrogen cyanide is generated. This most toxic form of cyanide can be fatal to humans in a few minutes at concentrations of 300 ppm. Soluble cyanides, while less toxic, are also fatal to sensitive species of fish at levels between 0.05 and 0.10 mg/l and are rapidly fatal for most fish species above 0.2 mg/l.<sup>(5)</sup> Further evidence of the potential hazard of disposed cyanide wastes is the fact that cyanide salts and complexed cyanides may: (1) migrate from disposal sites in substantial concentrations, (2) may be improperly managed, and (3) have proved hazardous to human health in actual waste management incidents.\*

1. Hazards via a Groundwater Exposure Pathway

These wastes contain high concentrations of cyanide, a highly toxic substance. As illustrated in Table 3A above,

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\*Additional damage incidents are described in the electroplating waste background document.

cyanide concentrations in these wastes may vary from 38 ppm to 350,000 ppm -- highly elevated concentrations in light of cyanide's extreme toxicity (see App. A and pp. 27-28). The U.S. Public Health Service recommended standard for cyanide in drinking water, for example, is 0.2 mg/l (App. A). Thus, these cyanide concentrations in and of themselves are of considerable regulatory concern.

Furthermore, cyanide is present in these wastes in soluble form. Table 4 contains simulated leachate extract data for the waste streams contained in Table 3A. The extraction procedure is based upon the acidic environment utilized in the Subtitle C EP. This data indicates that the complexed cyanides tend to be relatively soluble and the cyanide salts were highly soluble in this environment. In all cases, cyanide leached from the waste in concentrations exceeding the U.S. Public Health Service recommended standard, in most cases, by many orders of magnitude. Thus, cyanide is fully capable of migrating from disposed wastes.

Cyanide would be capable of migrating from these wastes if improperly disposed, for example, if disposal occurred in areas with permeable soils, or if adequate leachate control measures are not adopted. The migrating cyanide is likely to be highly mobile, since cyanides have been shown to be extremely mobile in the soil environment. pH appears to influence the mobility, with greater mobility at high pH. (14)

Table 4  
LEACHABLE CYANIDE WATES(2)

<u>Industry</u>	<u>Source *</u>	<u>Type of Waste/Form**</u>	<u>Annual Disposal in Gallons</u>	<u>Cyanide Concentrations ppm</u>	<u>Leachable Cyanide/ Metals (pH 5.5 Conditions) Within These Wastes (ppm)</u>
	(Cyanide Salts)				
Metal Heat Treating	Quenching Bath Sludge and Spent Solution	Potassium and Sodium Cyanide/ Solid***	3,000	92,300	--
Metal Heat Treating	Quenching Bath Sludge	Potassium and Sodium Cyanide/ Sludge	13,200	8,530	8,530
Electroplating	Spent Cleaning Bath Solution	Sodium Cyanide/ Solution	22,500	350,000	18,000
Electroplating	Spent Cleaning Bath Solution	Cyanide Salts/ Solution	14,000	38	28
Electroplating	Spent Plating Bath Solution	Cyanide Salts/ Sodium	6,600	14,547	9,048
Electroplating	Plating Bath Sludge	Metal Salts/ Sludge	1,000	64	49
	(Complexed Cyanides)				
Electroplating	Plating Bath Treatment Sludge	Complex Metal Cyanide/ Solution	15,600	80	0.5
Electroplating	Spent Plating Bath Solution	Complex Metal Cyanide/ Solution	6,600	14,329	119

Table 4 (Continued)

<u>Industry</u>	<u>Source *</u>	<u>Type of Waste/Form**</u>	<u>Annual Disposal in Gallons</u>	<u>Cyanide Concentrations ppm</u>	<u>Leachable Cyanide/ Metals (pH 5.5 Conditions) Within These Wastes (ppm)</u>
Electroplating	Spent Plating Bath Solution	Complex Metal Cyanide/Solution	36,000	2,000	80
Electroplating	Plating Bath Treatment Sludge	Complex Metal Cyanide/Solution	12,000	1,681	170
Metal Heat Treating	Quenching Waste-water Treatment Sludge	Complex Metal Cyanide/Solids***	6,600	26,803	915
Metal Heat Treating	Quenching Waste-water Treatment Sludge	Complex Metal Cyanide/Sludge	5,500	8,400	9.3

\*Source descriptions included in special waste disposal applications were not always the same as those presented in the listing<sup>(1)</sup>. An attempt was made to classify the waste into appropriate category.

\*\*These descriptions were taken directly from the special waste disposal applications<sup>(2)</sup>.

\*\*\*Solid cyanide wastes are placed in drums and disposed of. Solid waste quantities are expressed in gallons related to the size of the drum used to containerize waste for disposal.

Even clay liner systems may not adequately impede migration, as in the presence of water, montmorillonite clays (which have high surface areas) sorbed cyanide only weakly.(15) Cyanide has also been shown to move through soils into groundwater.(16) In light of the extreme toxicity of this waste constituent in the environment, its migratory potential in both salt and complexed form, and its environmental persistence and mobility, it strongly appears that waste mismanagement can result in substantial potential hazard.

Certainly the Administrator cannot with assurance state that cyanide will not migrate from these wastes and persist in the environment; yet such assurance is required to justify a decision not to list these wastes.

In any case, actual damage incidents involving cyanide-containing wastes, including some of the wastes listed here, confirm that cyanide can migrate, persist, and contaminate groundwater, public drinking water, soil, and vegetation. For example, a landfill site in Gary, Indiana, in which large quantities of cyanide electroplating wastes have been disposed, has leached into groundwater supplies.(17)

A total of 1,511 containers (mostly 55 gallon and 30 gallon drums) of industrial waste containing cyanides, heavy

metals, and miscellaneous other materials were disposed of improperly on a farm near Bryon, Illinois. Leachate entering nearby surface water was responsible for the death of three cows and substantial damage to wildlife (birds, downstream aquatic community, stream bottom-dwelling organisms) and local vegetation. Pathological examinations established that the cattle died of cyanide poisoning.(12)

In 1965, unlined lagoons in Columbia County, Pennsylvania, caused contamination of private wells in the area. The lagoons were leaking plating wastes containing cyanide, copper, nickel alkylbenzenesulfonate, and phosphate.(12)

A landfill in Monroe County, Pennsylvania, that accepts plating process wastes such as hydrocyanic acid, has created a groundwater pollution problem in the area.(12)

Between 1962 and 1972 in Lawrenceburg, Tennessee, an industry dumped up to 5,000 gallons of untreated metal plating waste daily into trenches near the city dump. Trace quantities of cyanide were measured in private wells and in an adjacent drinking water supply.(12) More recently, cyanide wastes were disposed down boreholes in Pittston, Pennsylvania, which discharged directly into a nearby waterway.(13)

## 2. Reactivity Hazard

Cyanide salt-containing wastes (although not complexed cyanide wastes) pose a reactivity hazard as well. These are cyanide bearing wastes which when exposed to mild acidic conditions react to release toxic hydrogen cyanide gas, and

thus possess the characteristic of reactivity (see §261.23 (a)(5)).

Documented damage incidents resulting from mismanagement of wastes from disposal of cyanide salts are presented below:

Damage Resulting from Reactivity of Wastes

- (1) A tank truck emptied several thousand gallons of cyanide waste onto refuse at a sanitary landfill in Los Angeles County, California. Another truck subsequently deposited several thousand gallons of acid waste at the same location. Reaction between the acid and the cyanide evolved large amounts of toxic hydrogen cyanide gas. A potential disaster was averted when a local chlorine dealer was quickly called to oxidize the cyanide with hydrogen chlorine solution.<sup>(12)</sup> Hydrogen cyanide gas can be fatal to humans in a few minutes at a concentration of 300 ppm. The average fatal dose is 50 to 60 mg.
- (2) A standard procedure at a Southern California disposal site for handling liquid wastes containing cyanides and spent caustic solutions was to inject these loads into covered wells dug into a completed section of a sanitary landfill. Routine air sampling in the vicinity of the wells detected more than 1000 ppm HCN. No cyanide was detected during addition of the spent caustic to a new well. On

the basis of these discoveries, use of the wells was discontinued. The cyanide gas was apparently formed in the well as a result of lowering of the pH of the waste by CO<sub>2</sub> and organic acids produced in the decomposition of refuse.(12)

#### V. HEALTH EFFECTS

The toxicity of both cyanides and hydrogen cyanide have been well documented. Cyanide in its most toxic form can be fatal to humans in a few minutes at a concentration of 300 ppm. Cyanide is also lethal to freshwater fish at concentrations as low as about 50 mg/l and has been shown to adversely affect invertebrates and fish at concentrations of about 10 mg/l. Hydrogen cyanide is also extremely toxic to humans and animals, causing interferences with respiration processes leading to asphyxiation and damage to several organs and systems. Toxic effects have also been reported at the very low exposure level of less than 1 mg/kg.(15,16)

The hazards associated with exposure to cyanide and hydrogen cyanide have also been recognized by other regulatory programs. Congress listed cyanide as a priority pollutant under §307(a) of the Clean Water Act of 1977. In addition, the U.S. Public Health Service established a drinking water standard of 0.2 mg/l as an acceptable level for cyanide in water supplies. The Occupational Safety and Health Administration (OSHA) has established a permissible exposure limit for KCN and NaCN at 5 mg/m<sup>3</sup> as an eight-hour time-weighted average.

Additionally, the OSHA permissible limit for exposure to HCN is 10 ppm (11 mg/m<sup>3</sup>) as an eight-hour time-weighted average. DOT requires a label stating that HCN is a poisonous and flammable gas.

Finally, final or proposed regulations of the states of California, Maine, Maryland, Massachusetts, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define cyanide containing compounds as hazardous wastes or components thereof.(17)

A more detailed discussion of the health effects of cyanide is contained in Appendix A.

V. REFERENCES

1. U.S. EPA. The manufacture and use of selected cyanides. EPA. No. 560/6-76-012. NTIS PB No. 251 820. April, 1976.
2. U.S. EPA. Composite of State Regulations Files. Special wastes disposal applications. Results of leachate tests on cyanide containing wastes from Illinois, Iowa, Kansas and Pennsylvania. Hazardous Waste State Programs, WH-565, U.S. EPA., 401 M St., S.W., Wash., D.C. 20460.
3. Cotton, F. A. and G. Wilkinson. Advanced inorganic chemistry. John Wiley & Sons, Inc., New York. 1979.
4. U.S. EPA. Production and use of cyanide. NTIS PB No. 297 606. 1978.
5. U.S. EPA. Quality criteria for water. NTIS PB No. 263 143. July, 1976.
6. Personal communication. W. Webster, U.S. EPA, to K. Crumvine, U.S. EPA. January 17, 1980.
7. U.S. EPA. Development document for proposed existing source pretreatment standards for the electroplating point source category. EPA No. 440/1-78/085. February, 1978.
8. U.S. EPA. Industrial process profiles for environmental use: Chapter 24, The iron and steel industry. EPA No. 600/2-77-023X. NTIS PB No. 266 226. February, 1977.
9. Not used in text.
10. U.S. EPA. Assessment of industrial hazardous waste practices special machinery manufacturing industries. EPA No. SW-141C. NTIS PB No. 265 981. March, 1977.
11. U.S. EPA. Development document for effluent limitations guidelines and new source performance standards for the iron and steel foundry industry. Office of Water & Waste Management, U.S. EPA. 401 M St., S.W., Washington, D.C. 20460. July, 1974.
12. U.S. EPA. Open Files. Hazardous Site Control Branch. WH-548. U.S. EPA, 401 M Street S.W., Washington, D.C. Contact Hugh Kauffman. (202) 245-3051.
13. Philadelphia Enquirer. Series of articles related to Pittston cyanide disposal. October 15-26, 1979.

14. Alessi, B.A., and W.H. Fuller. The mobility of three cyanide forms in soil. In: Residual management by land disposal. W.H. Fuller, ed. NTIS PB No. 256 768. 1976.
15. Cruz, M., et. al. Absorption and transformation of HCN on the surface of calcium and copper montmorillonite. Clay Minerals. 22:417-425. 1974.
16. U.S. EPA. The prevalence of subsurface migration of hazardous chemical substances at selected industrial waste land disposal sites. EPA No. 520/SW-634. NTIS PB No. 272 973. 1977.
17. Chemical & Engineering News. Editors Newsletter. November 17, 1979.

Response To Comments  
on Proposed Listings (December 18, 1978)

1. One commenter suggested that the listings of "Spent or waste cyanide solutions or sludges" should be modified so as to include solutions or sludges containing small amounts of cyanide formed during one or more proces operations. The following language was recommended:

"Spent or waste cyanide solutions or sludges  
resulting from cyanide-based processes (R,T)"

  - ° The Agency agrees with the commenter that solutions or sludges that contain minute quantities of cyanide should not and are not intended to be included in the above listing. However, to limit the listing to just those processes which result from cyanide-based processes may leave out several waste streams from RCRA control wich could present a problem, if improperly managed. For example, during blast furnace operations nitrogen, water and carbon combine to produce hydrogen cyanide. Desulfurization scrubbers installed on many of the blast furnace stacks scrub HCN scrubber liquor is rarely treated. Thus, if the scrubber liquor is dewatered, the cyanide is likely to end up in the sludge at concentrations high enough to be of concern (see discussion under Coke Oven and Blast Furnace, p. 15, for more details).
2. A number of comments suggested that the definition of cyanide bearing wstes should distinguish between "free cyanide" and "ferro cyanide", since the latter would not be available to generate hydrogen cyanide under mild, acidic, or basic conditions.
  - ° The Agency agrees that only cyanide salt-containing wastes pose a reactivity hazard, and the listing descriptions reflect this distinction, since no complex cyanide wastes are listed for reactivity.

Response to Comments - Spent Waste Cyanide Solutions and Sludges [Interim Final Regulation, May 19, 1980]

A number of comments have been received with respect to wastes F007 to F016 (Spent plating bath solutions from electroplating operations; Plating bath sludges from the bottom of plating baths from electroplating operations; Spent stripping and cleaning bath solutions from electroplating operations; Quenching bath sludge from oil baths from metal heat treating operations; Spent solutions from salt bath pot cleaning from metal heat treating operations; Quenching wastewater treatment sludges from metal heat treating operations; Flotation tailings from selective flotation from mineral metals recovery operations; Spent cyanide bath solutions from mineral metals recovery operations; and Dewatered air pollution control scrubber sludges from coke ovens and blast furnaces).

1. A number of commenters have indicated that the Agency, in listing wastes F007 to F013, has inadvertently included wastes generated by processes that do not use cyanide or cyanide compounds and, thereby, describe wastes that do not contain cyanide salts or complexes. Therefore, the commenters recommend that the listing descriptions for wastes F007 to F013 to be modified to make it clear that only those processes which use

cyanide salts or complexes would be covered by the listing.\*

The Agency agrees with the commenters. In promulgating these waste listings, the Agency only intended to describe wastes that may contain cyanide salts or complexes. Therefore, the Agency has redefined the subject wastes to indicate that only wastes from processes utilizing cyanides are included. Specific wording changes in the listing description are set out below (the changes to these definitions are underlined):

EPA Hazardous  
Waste Number

Hazardous Waste

F007

Spent cyanide plating bath solutions from electroplating operations (except for precious metals electroplating spent cyanide plating bath solutions)

F008

Plating bath sludges from the bottom of plating baths from electroplating operations where cyanides are used in the process (except for precious metals electroplating plating bath sludges)

\*Among the processes cited as not always using cyanides are:  
(1) aluminum anodizing process (electroplating), (2) chemical conversion coating operations (electroplating), (3) tin plating on carbon steel (electroplating), (4) zinc plating (segregated basis) on carbon steel (electroplating), (5) aluminum or zinc-aluminum plating carbon steel (electroplating), (6) cleaning/stripping associated with tin, zinc and aluminum plating on carbon steel (electroplating), (7) metal heat treating operations, and (8) selective flotation from mineral metals recovery operations.

EPA Hazardous  
Waste Number

Hazardous Waste

F009	Spent stripping and cleaning bath solutions from electroplating operations <u>where cyanides are used in the process</u> (except for precious metals electroplating spent stripping and cleaning bath solutions)
F010	Quenching bath sludge from oil baths from metal heat treating operations <u>where cyanides are used in the process</u> (except for precious metals heat-treating quenching bath sludge)
F011	Spent <u>cyanide</u> solutions from salt bath pot cleaning from metal heat treating operations (except for precious metals heat-treating spent solutions from salt bath pot cleaning)
F012	Quenching wastewater treatment sludges from metal heat treating operations <u>where cyanides are used in the process</u> (except for precious metals heat-treating quenching wastewater treatment sludges)
F013	Waste is being removed from the list- see No. 4 of this section for more details

2. One commenter objected to the inclusion of solutions and sludges extracted or emanating from precious metals electroplating and metal heat treating operations. The commenter pointed out that these solutions and sludges are richly impregnated with precious metals--gold, silver, platinum and its derivatives, or rhodium and thus are never discarded (to the

commenter's knowledge), but are always sent to metal recovery or reclamation. Therefore, the commenter argues that these solutions and sludges are not "solid wastes", as that term is defined in §261.2 of the Subtitle C regulations.

In evaluating the commenters arguments, the Agency agrees with the commenter that both the solutions and sludges extracted from precious metals electroplating and metal heat treating operations are not solid wastes, and therefore, have been excluded from the hazardous waste listings F007 to F012. The primary argument on which the Agency based its decision is the extremely high value of the precious metals and the fact that most if not all of these facilities could not afford to discard these solutions and sludges. As pointed out by the commenters, these solutions and sludges are never discarded, thus, these materials do not meet the current definition of solid waste (45 FR 33119). Therefore, the Agency has excluded solutions and sludges from precious metals electroplating and heat treating operations from these listed waste categories. Residues from reclamation of these solutions and sludges are solid wastes, however, and must be tested against the characteristics of hazardous waste to determine if they are hazardous.

We note further that the definition of "solid waste" may be amended in the future, and that these materials may be solid wastes under the amended definition. In that event,

we do not intend to repropose this listing for comment, in light of our earlier proposal and interim final promulgation when the opportunity for comment was utilized fully.

3. A number of commenters argued that the Agency should differentiate between the form of cyanide present in the waste (i.e., complex cyanides vs. free cyanides). The commenters point out that complex cyanides are considerably less toxic than free cyanides (the commenters do not disagree that free cyanides are toxic). They argue in addition that complex cyanides are generally insoluble and environmentally stable. Therefore, the commenters recommend that wastes listed for complexed cyanides be removed from the hazardous waste listings.

The Agency disagrees with the commenters. First of all, it should be pointed out that the Agency has already differentiated between the form of cyanide present in the waste i.e., only cyanide salt-containing wastes (free cyanides) are listed as posing a reactivity hazard.

Second, although complexed cyanides are less toxic than free cyanides, this simple statement does not adequately address the potential for harm posed by complexed cyanide-bearing wastes because complexed cyanides undergo photodecomposition resulting in extremely toxic hydrogen cyanide and free cyanide decomposition by-products.\*/

\*/ These toxic photodecomposition residuals (chiefly HCN) have been shown to be resistant to naturally occurring wavelengths reaching the earth's surface. (Frank, S.N., and D.J. Bard. 1977. Heterogeneous photocatalytic oxidation of cyanide ion in aqueous solution of titanium dioxide powder. Jour. Amer. Chem. Soc. 99(1): 303-304. Thus, these residuals will not photolyse further so that this degradation mechanism will not further affect toxicity in waste management settings.

This phenomenon is especially well documented for iron cyanides, the most prevalent form of complexed cyanide in the wastes listed here. (See Ecological Analysts, Inc., Cyanide, an Overview and Analysis of the Literature on Chemistry, Fate, Toxicity, and Detection in Surface Waters, prepared for the Inter-Industry Cyanide Group, and sources there cited (June, 1979). While no photodegradation rate constant is indicated in these sources, it has been shown in laboratory experiments that the rate of generation of hydrogen cyanide and free cyanide via photodecomposition of complexed cyanides exceeds the rate of cyanide loss from solution via volatilization. Thus, we can clearly envision situations where mismanaged wastes containing complexed cyanides cause substantial environmental harm due to photolysis and subsequent migration of HCN and free cyanides.

Damage incidents involving disposal of complexed cyanide-containing wastes bear out our concern. Thus, a series of massive fish kills have been reported presumably caused by the photodecomposition of iron cyanides. (See Doudoroff, 1976, Toxicity to Fish of Cyanide and Related Compounds--A Review (prepared for U.S. EPA, EPA 600/3-76-038). In one such incident, fish mortalities occurred in the summer of 1949 in Tulpehocken Creek, Lebanon County, Pennsylvania, and were believed to have been due to pollution escaping from a leaking waste-treatment lagoon accepting complexed cyanide wastes. "Appreciable amounts of ferro- and ferricyanide"

were said to have been found in the seepage from the waste-treatment lagoon and in a heavy silt deposit in the stream bottom. Cyanide was found in the tissues of dead fish in amounts believed to have been sufficient to have caused death, and local residents reported that all the fish mortalities occurred at midday on bright, sunny days (emphasizing the role of photodecomposition).

Therefore, the Agency will continue to list wastes which contain complexed cyanides since they do have the potential to migrate, photodecompose and generate HCN and present a substantial hazard to human health and the environment.

4. A large number of commenters have also objected to the inclusion of "flotation tailings from selective flotation from mineral metals recovery operations" on the hazardous waste list. The commenters argue that the Agency's rationale for listing this particular waste is objectionable both on procedural grounds and technical grounds. With respect to the procedural arguments, the commenters claim that this particular listing was never proposed as a hazardous waste prior to its listing, thus, the requirements under the Administrative Procedure Act has not been followed.

The commenters also argued substantively that available scientific and technical data do not support listing this waste as hazardous. Their specific claims are:

- a. Nature of the Toxicity: Flotation tailings will only contain complex cyanides, not highly toxic free cyanides.
- b. Concentration of Cyanide Waste: Concentration of cyanide in the tailings is so low as not to pose any threat. A number of commenters provided specific analytical data on the concentration of of cyanide in the waste. These concentrations ranged from 10 ug of  $CN^-/l$  to 1 mg of  $CN^-/l$
- c. Potential to Migrate: Complex cyanides are generally stable and even when they do disassociate the percentage of free cyanide produced from the complex cyanide is small.
- d. Persistence: Cyanides have a low degree of persistence in the environment.
- e. Potential to Degrade into Non-harmful Constituents: Cyanide is amenable to a number of natural treatment methods including air oxidation, sunlight and biodegradation.
- f. Bioaccumulation: Cyanide does not bioaccumulate.
- g. Improper Management: It is virtually impossible to improperly manage disposal of this waste stream (no explanation was provided concerning this statement).
- h. Reported Damage: No known cases of damage to human health or the environment caused by cyanide from tailings are cited in the background document.

Therefore, the commenters recommend that the Agency remove its classification of flotation tailings as a hazardous waste.

The Agency strongly disagrees with the commenters that the Agency has failed to follow the procedures required by the Administrative Procedures Act (APA). On December 18, 1978, the Agency proposed a list of approximately 200 hazardous wastes, including "Spent or waste cyanide solutions or sludges (R,T)" (see proposed §250.14(a) [45 FR at 58957]). As a result of this proposed listing, a number of comments were received which suggested that the Agency list those specific cyanide wastes of regulatory concern, instead of a listing solely on a generic basis. In response to comments, the Agency therefore listed ten (10) specific cyanide-containing wastes, including the flotation tailings. Additionally, in promulgating this particular waste interim final on May 19, 1980 (45 FR 33123), the Agency allowed an additional opportunity to comment before promulgating the listing as a "final-final" regulation. Therefore, the Agency believes that sufficient opportunity for comment was provided.

However, we are persuaded by the commenters technical arguments, and therefore will remove waste F013 (flotation tailings from selective flotation from mineral metals recovery operations) from the hazardous waste list. We are convinced that cyanide concentrations in this waste stream ordinarily are too low to be of regulatory significance. Analytical

data submitted by commenters and results of a study conducted by Battelle,\* indicate that concentration of cyanides found in this waste are very low and are present in a stable form, so that migration of free cyanides from this waste is unlikely to occur.\*\* We thus do not believe that this waste would pose a substantial hazard to human health and the environment, if improperly managed.

5. One commenter also argued that waste F014, "Cyanidation wastewater treatment tailing pond sediment from mineral metals recovery operations" is not hazardous. The commenter raised many of the same arguments advanced to challenge the listing of flotation tailings (F013), but provided no analytical data in support.

After again reviewing the various processes that would use cyanide (cyanidation) and generate a cyanidation wastewater treatment tailing pond sediment, the Agency continues to believe that this waste will contain significant concentrations of cyanide, based on the large quantity of cyanides disposed. For example, data provided in the listing background document indicates that between 1-10 kkg of complexed cyanides are disposed of by these facilities. We thus will continue

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\*Mezey, E.J., G.R. Smithson, and James F. Shea, Draft Final Report on Phase II, "Treatability and Alternatives for NaCn for Flotation Control," IERL/EPA, Cincinnati, Ohio. January 31, 1980.

\*\*Analysis of the flotation tailings for cyanides provided by the commenters were  $<.01 \text{ ug CN}^-/\text{g}$ ,  $.58 \text{ mg CN}^-/\text{l}$  and  $1 \text{ mg of CN}^-/\text{l}$ . Data provided in the Battelle Report indicated that most if not all mines using cyanide use cyanide in "almost starvation amounts."

to include this particular waste in Part 261.31. In addition, the Agency believes that the conditions of disposal/storage are ripe for the complexed cyanides to photolyze to free cyanides which are extremely toxic and highly mobile due to the practice in the industry to use sunlight as part of the treatment process for cyanides (see pg. 12).

Moreover, we note the absence of any supporting data in the comment showing empirically that this waste typically contains insignificant concentrations of cyanide. The Agency will continue to list this waste until such a showing is made.

6. Another commenter objected to the inclusion of waste F016, "Dewatered air pollution control scrubber sludges from coke ovens and blast furnaces." The commenter first argued that the cyanide compounds present in coke oven and iron blast furnace scrubber sludges are iron cyanide complexes which are "non-toxic." The commenter then pointed to several studies commissioned by EPA to evaluate the potential hazardousness of steel industry wastes. The first study\* concluded that the level of heavy metals, cyanide and phenols in iron blast furnace dust and sludge leachate, were less than 10 times the 1977 EPA Drinking Water Quality Standard. The other study\*\* also concluded that iron blast furnace sludge was not found to leach toxic constituents in significant concentrations. Furthermore, the commenter argued that while some pertinent

leachate data for a coke oven sludge is presented, the concentration of total cyanide found in the coke oven leachate is relatively small (0.613 mg/l).\*\*\* Finally, a number of steel companies analyzed the eleuate of their waste by means of the EP test and showed an insignificant concentration of total cyanide in the leachate.\*\*\*\* Therefore, the commenter recommends that this waste be deleted from §261.31.

After reviewing these data, it appears that these wastes contain small concentrations of cyanide, and that the cyanide present has very limited migratory potential. We therefore are not listing this waste stream as hazardous. It should be pointed out that the Agency is making this decision to de-list all scrubber sludges from blast furnaces and coke ovens mainly on data from iron blast furnaces. However, the Agency would expect to find similar concentrations of cyanide from both blast furnaces and coke ovens because the underlying

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\* Enviro Control, Inc., Hazardous Waste Listings: Fully Integrated Steel Mills (Aug. 1978), prepared for EPA under Contract No. 68-01-3937.

\*\* Calspan Corp., Assessment of Industrial Hazardous Waste Practices in the Metal Smelting and Refining Industry, Volume III, Ferrous Smelting and Refining at 17 (April 1977), prepared for EPA, PB 276161

\*\*\* Composite of State Files of "Special Waste Disposal Application." 1976-1979. Results of Lechate Tests on Cyanide Wastes from Illinois, Iowa, Kansas, and Pennsylvania.

\*\*\*\* Analysis of the eleuate from various iron blast furnace sludges extracted by means of the EP test were 0.091 mg/l, 0.086 mg/l and 0.005 mg/l of total cyanide.

process is essentially similar. If the Agency identifies data to contradict this assumption, we will consider bringing appropriate sub-categories of these wastes back into the hazardous waste regulatory control system.

## LISTING BACKGROUND DOCUMENT

### Chromium Pigments and Iron Blues

Wastewater treatment sludge from the production of chrome yellow and orange pigments (T)

Wastewater treatment sludge from the production of molybdate orange pigments (T)

Wastewater treatment sludge from the production of zinc yellow pigments (T)

Wastewater treatment sludge from the production of chrome green pigments (T)

Wastewater treatment sludge from the production of chrome oxide green pigments (anhydrous and hydrated) (T)

Wastewater treatment sludge from the production of iron blue pigments (T)

Oven residue from the production of chrome oxide green pigments (T)

#### Summary of Basis for Listing

The above listed wastewater treatment sludges are generated when wastewaters from chromium pigments production are treated to remove heavy metals. Oven residue from hydrated chromic oxide manufacture is generated when the raw materials are heated together to form the pigment product. The Administrator has determined that these wastewater treatment sludges and oven residues are solid wastes which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed and therefore should be subject to appropriate

## **Inorganic Chemicals**

management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. These wastewater treatment sludges contain substantial amounts of the toxic metals lead and chromium (to some extent in hexavalent form) and also contain ferric ferrocyanide when iron blue pigments are produced. The oven residue contains a substantial amount of hexavalent chromium.
2. If these wastes are managed improperly, toxic chromium and lead may leach from the waste and migrate to the environment. Ferrocyanide will decompose upon exposure to sunlight, releasing cyanides and hydrogen cyanide gas.
3. A significant quantity of these sludges is generated annually, and the amount is expected to increase. When industry wastewater treatment standards based on best practicable technology are implemented, approximately 4300 metric tons of sludge will be generated per year. Currently 50-60% of that amount is generated.
4. These wastes are frequently disposed of in unlined lagoons and landfills, or dumped in the open. These management practices may not be adequate to prevent toxic constituents from being released to the environment.

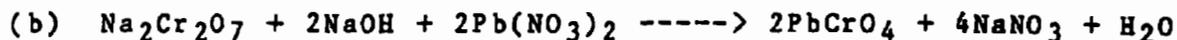
#### Profile of the Industry (1,2)

Chrome pigments are used extensively in paints, printing ink, floor covering products and paper. They may also be used in ceramics, cement and asphalt roofing. Eleven plants currently manufacture chromium pigments; two also manufacture iron blue pigments. Individual plant production rates range from a low of 9 metric tons per day to a high of 79 metric tons per day. Total yearly industry-wide production is estimated at 64,500 metric tons; approximately 60% of that total is manufactured by two plants in the northeastern United States. All other plants are located in the midwest and south.

## Manufacturing Processes

### 1. Manufacture of Chrome Yellow and Orange Pigments

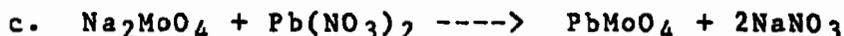
Chrome yellow and orange pigments are produced by reacting sodium dichromate, caustic soda and lead nitrate as follows (1):



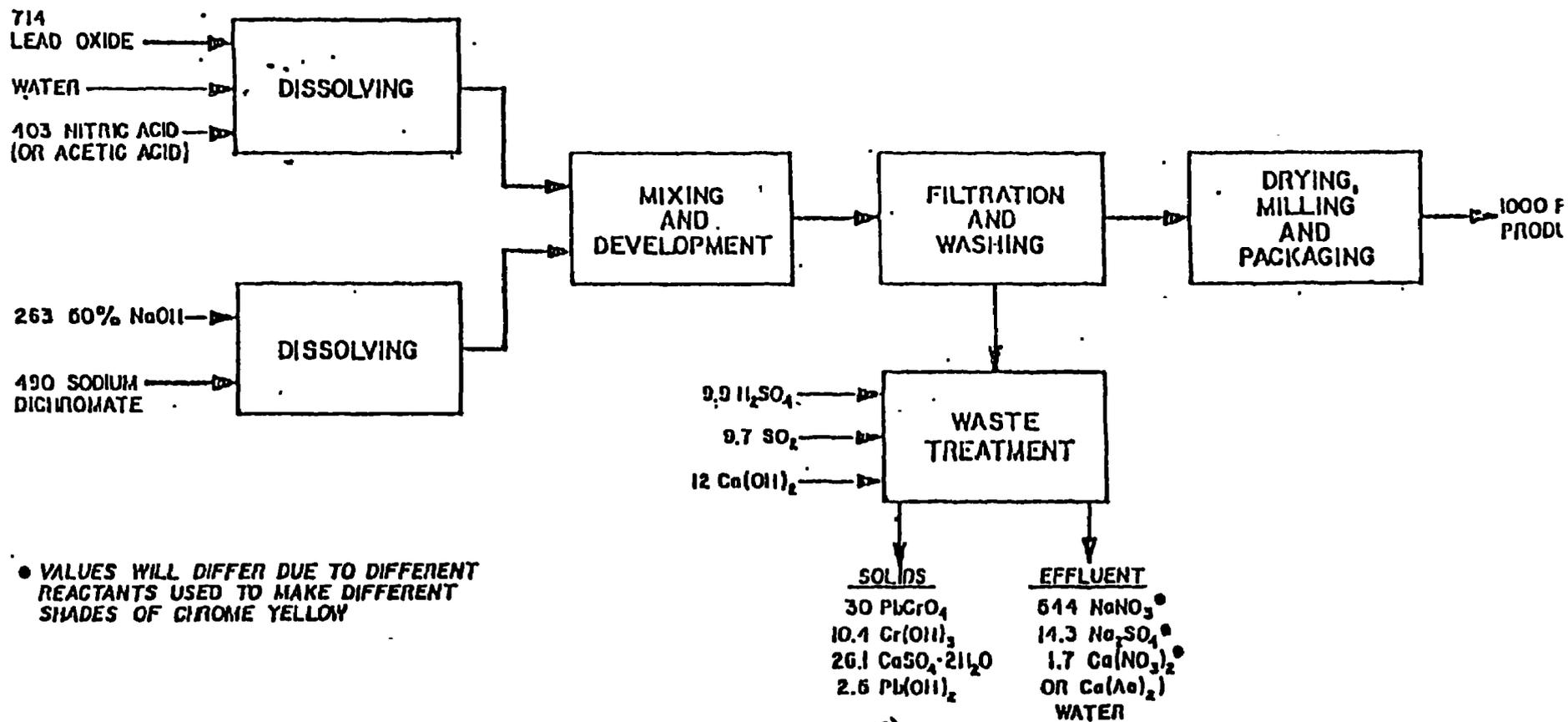
Lead chromate (a hexavalent chromate) is formed as a precipitate and is recovered by filtration, then treated, dried, milled and packaged. The filtrate, containing lead and hexavalent chromium compounds, is sent to a wastewater treatment facility. A process flow diagram is given in Figure 1 (3).

### 2. Manufacture of Molybdate Orange Pigments

Molybdate orange pigment is made by the co-precipitation of lead chromate ( $\text{PbCrO}_4$ ) and lead molybdate ( $\text{PbMoO}_4$ ). Molybdic oxide is first dissolved in aqueous sodium hydroxide; sodium chromate is then added. This solution is mixed and reacted with a solution of lead oxide in nitric acid. The reactions, all involving hexavalent chromium compounds, are as follows (1):

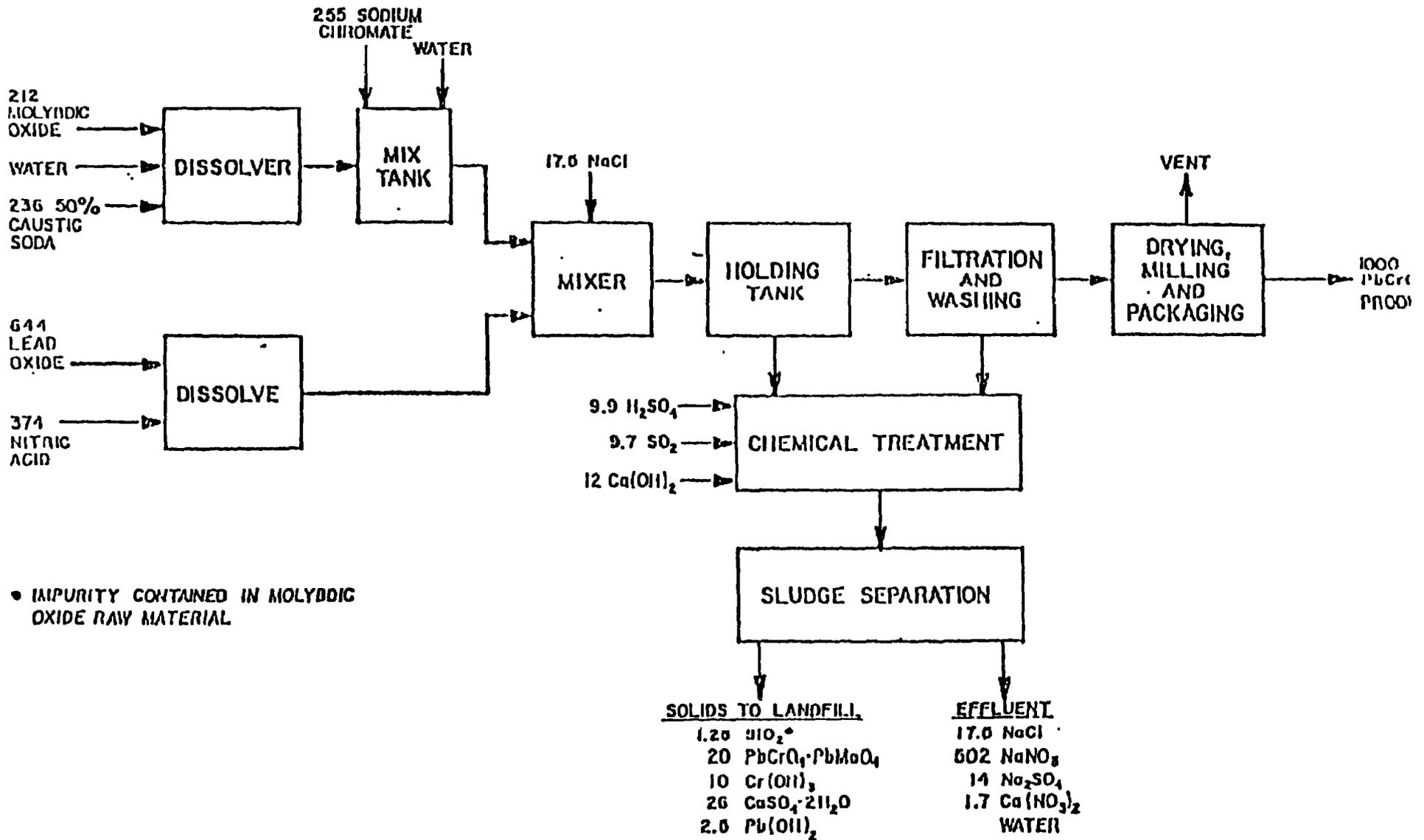


The precipitate (lead chromate and molybdate) is filtered, washed, dried, milled and packaged. The filtrate, containing lead and hexavalent chromium compounds, is sent to the wastewater



• VALUES WILL DIFFER DUE TO DIFFERENT REACTANTS USED TO MAKE DIFFERENT SHADES OF CHROME YELLOW

(s)  
FIGURE 1  
CHROME YELLOW MANUFACTURE



• IMPURITY CONTAINED IN MOLYBDIC OXIDE RAW MATERIAL

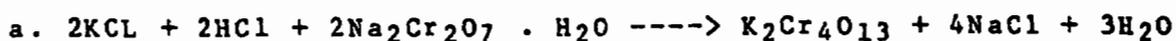
RF (3)

MOLYBDATE MANUFACTURE

treatment facility. A flow diagram is given in Figure 2 (3).

### 3. Manufacture of Zinc Yellow Pigments

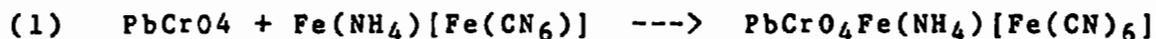
Zinc yellow pigment is a complex compound of the oxides of zinc, potassium and hexavalent chromium. It is produced by the reaction of zinc oxide, hydrochloric acid, sodium dichromate (a hexavalent chromium compound) and potassium chloride (1):



The product forms as a precipitate and is filtered, washed, dried, milled and packaged. The filtrate, containing hexavalent chromium compounds are sent to the wastewater treatment facility. A flow diagram is given in Figure 3 (3).

### 4. Manufacture of Chrome Green Pigments

Chrome green pigments are co-precipitates of chrome yellow and iron blues. They include a wide variety of hues, from very light to very dark green. Chrome green is produced by mechanically mixing chrome yellow and iron blue pigments in water. The coprecipitate formation of chrome green, a hexavalent chromium compound, is given by the following reaction (1):



The co-precipitate is filtered, dried, ground, blended and packed. The filtrate, containing lead and hexavalent chromium, is sent to wastewater treatment for removal of suspended pigment particles. Figure 4 gives a process flow diagram for the manufacture of chrome green (3).

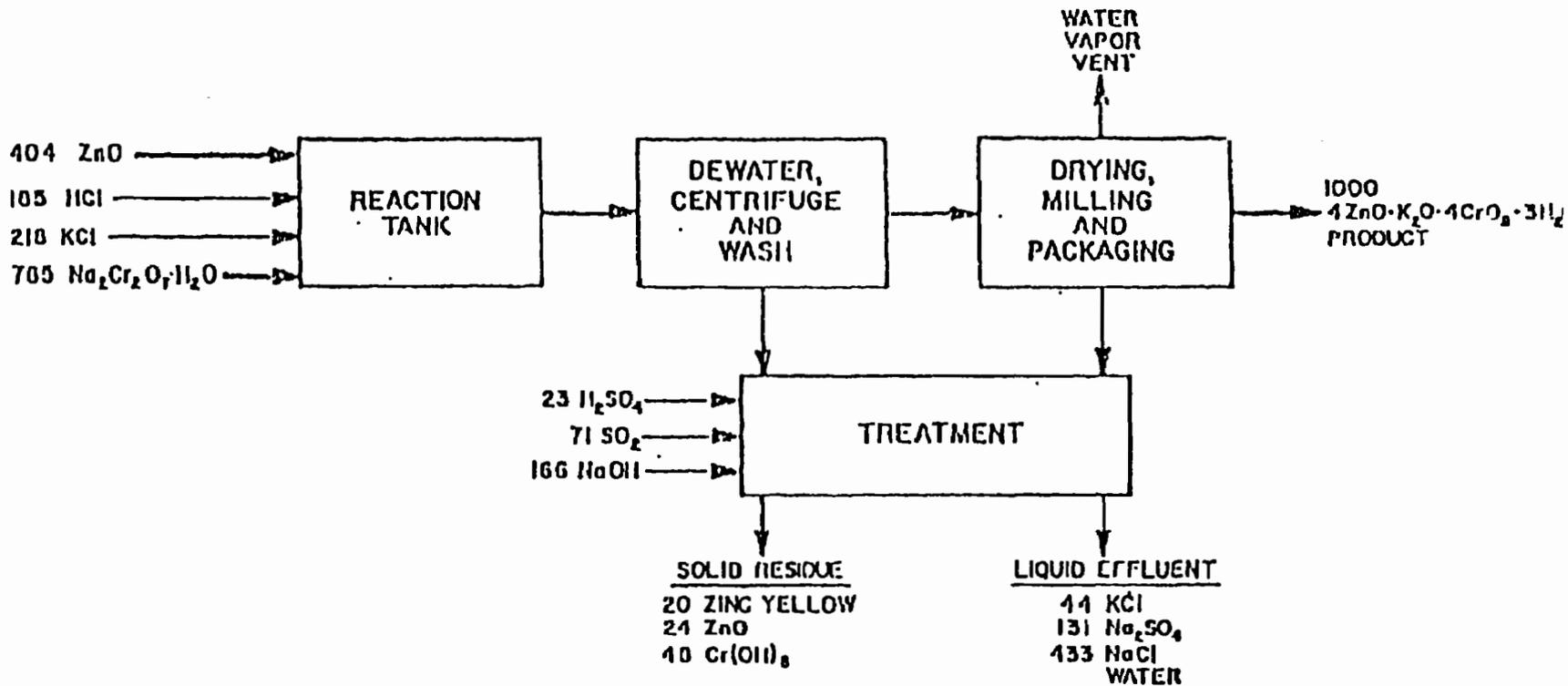
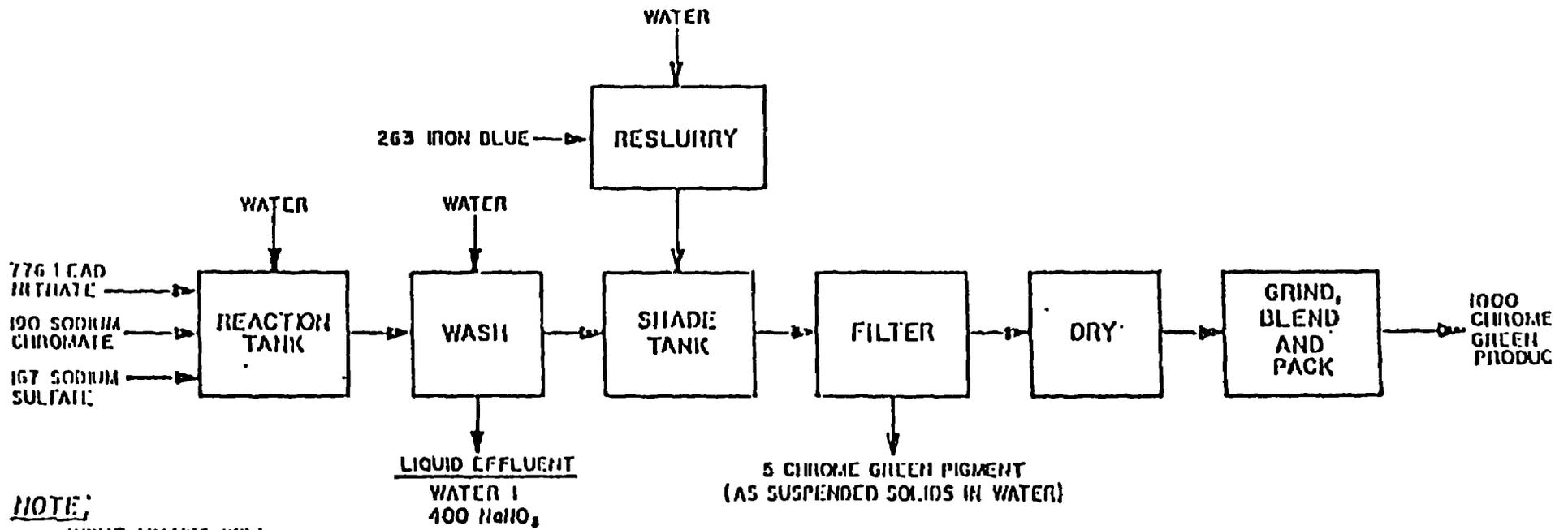


FIGURE 3<sup>(3)</sup>  
ZINC YELLOW MANUFACTURE



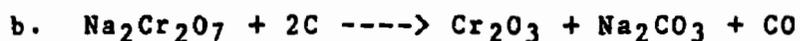
**NOTE:**

INPUT VALUES WILL VARY DEPENDING ON SHADE OF GREEN DESIRED.

FIGURE 4<sup>(3)</sup>  
CHROME GREEN MANUFACTURE

5. Manufacture of Anhydrous and Hydrated Chrome Oxide Green Pigments.

Anhydrous chrome oxide, a trivalent chromium pigment, is produced by the calcination of sodium dichromate, a hexavalent chromate, with sulfur or carbon according to either of the following reactions (1):



The recovered trivalent chromium oxide is slurried with water, filtered, washed, dried, and packaged. The washwaters, probably containing some unreacted hexavalent chromate materials, are sent to wastewater treatment. A process flow diagram is given in Figure 5 (3).

Hydrated (trivalent) chrome oxide is made by reacting sodium dichromate with boric acid as follows (1):



The raw materials are blended in a mixer, then heated in an oven at 550° C. Oven residues, which contain hexavalent and trivalent chromium, remain to be disposed of as wastes. The reacted material is slurried with water and filtered. The filtered solids are washed, dried, ground, screened and packaged. The filtrate and washwater are treated to recover boric acid. The waste stream from the boric acid recovery unit and washwaters from the filtration step, containing a hexavalent chromium compound, are sent to wastewater treatment. A process flow diagram is given in Figure 6 (3).

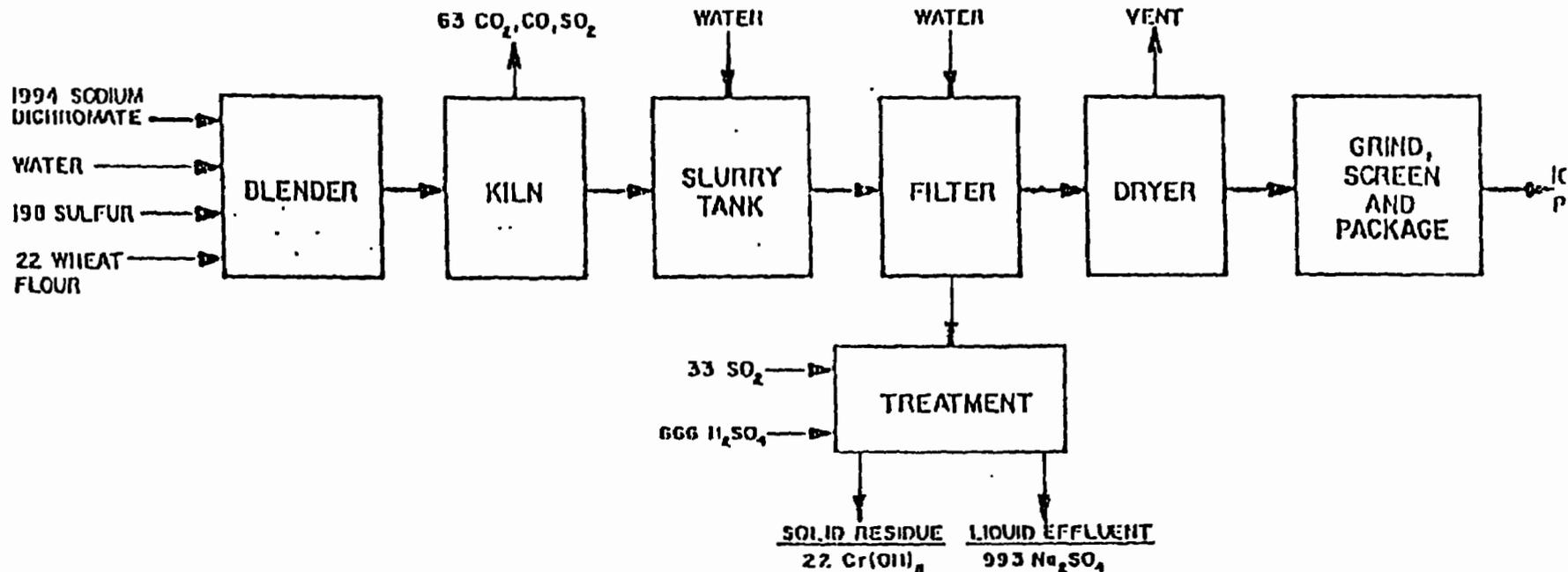


FIGURE 5<sup>(2)</sup>  
 ANHYDROUS CHROMIC OXIDE PIGMENT MANUFACTURE

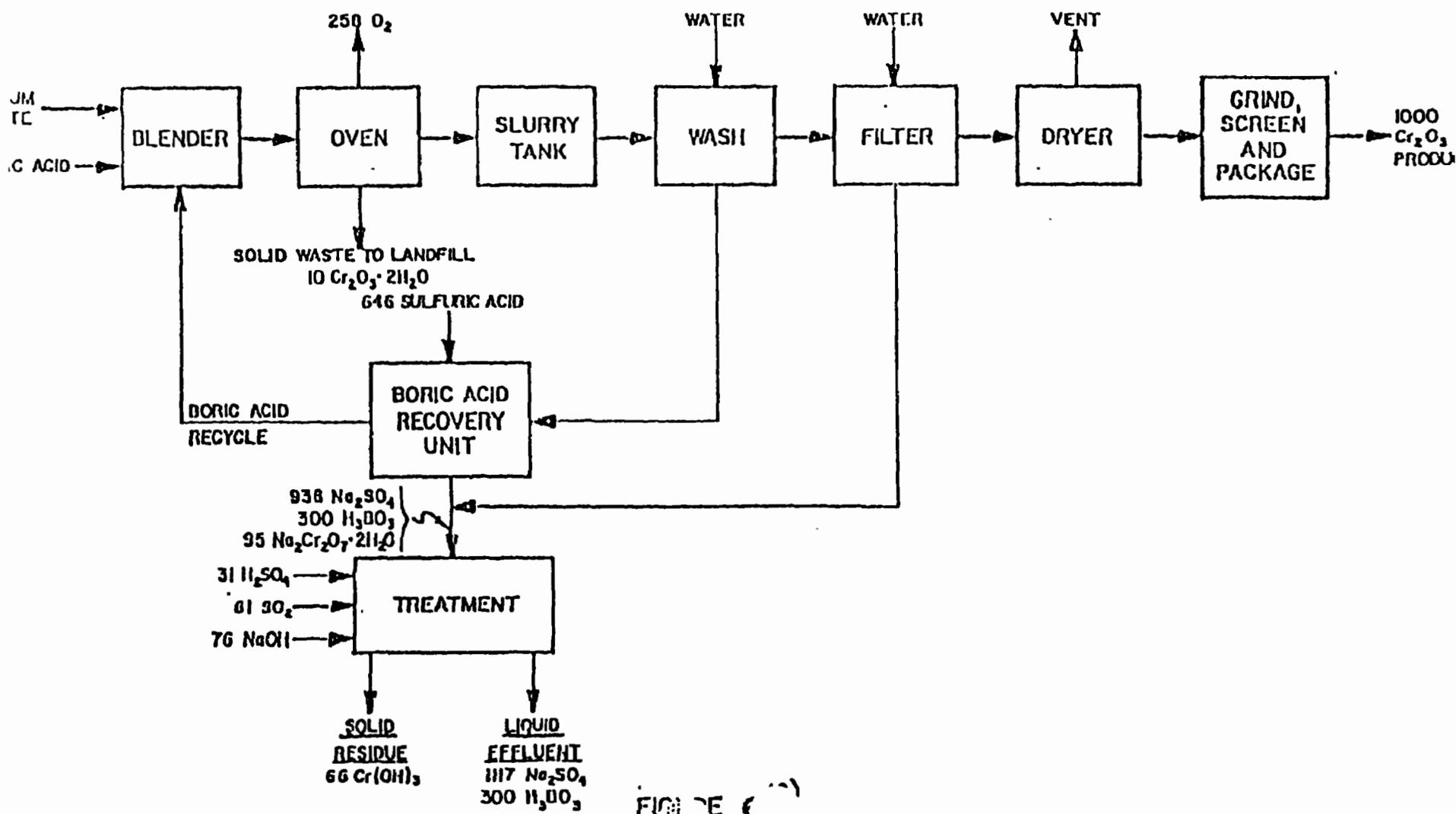


FIGURE 6  
HYDRATED CHROMIUM OXIDE MANUFACTURE

TABLE 1

Composition of Wastewater Treatment  
Sludge and Oven Residue from Chromium  
Pigments Production(3)

SOURCE OF SLUDGE	CONTAMINANTS IN SLUDGE Mass units/1000 mass units product.	Cr (VI) as% of total Cr
Production of Chrome Yellow and Orange Pigments	30 PbCrO <sub>4</sub> (Lead chromate) 10.4 Cr(OH) <sub>3</sub> (Chromium hydroxide) 2.5 Pb(OH) <sub>2</sub> (Lead hydroxide)	48.5
Production of Molybdate Orange Pigments	20 PbCrO <sub>4</sub> . PbMoO <sub>4</sub> (Molybdate Orange) 10 Cr(OH) <sub>3</sub> (Chromium hydroxide) 2.5 Pb(OH) <sub>2</sub> (Lead hydroxide)	23.4
Production of Zinc Yellow Pigments	20 4ZnO.K <sub>2</sub> O.4CrO <sub>3</sub> .3H <sub>2</sub> O (Zinc Yellow) 48 Cr (OH) <sub>3</sub> (Chromium hydroxide)	21.9
Production of Chrome Green Pigments	5 PbCrO <sub>4</sub> Fe(NH <sub>4</sub> )[Fe(CN) <sub>6</sub> ] (Chrome Green)	100
Production of Anhydrous Chromic Oxide Pigments	22 Cr(OH) <sub>3</sub> (Chromium hydroxide)	0
Production of Hydrated Chromic Oxide Pigments	66 Cr(OH) <sub>3</sub> (Chromium hydroxide)	0
Production of Iron Blue Pigments	25 Fe <sub>4</sub> (Fe(CN) <sub>6</sub> ) <sub>3</sub> (Ferric Ferrocyanide)	*
Oven Residue from Production of Chromic Oxide Pigments	10 Cr <sub>2</sub> O <sub>3</sub> .2H <sub>2</sub> O (Chromium Oxide)	0

\*Iron blue wastewater treatment sludge will contain chromium compounds when sodium chromate is used as an oxidizing agent. Generators, should they seek to delist their iron blue waste streams should thus address hexavalent chromium concentrations as well as cyanide concentrations in their wastes.

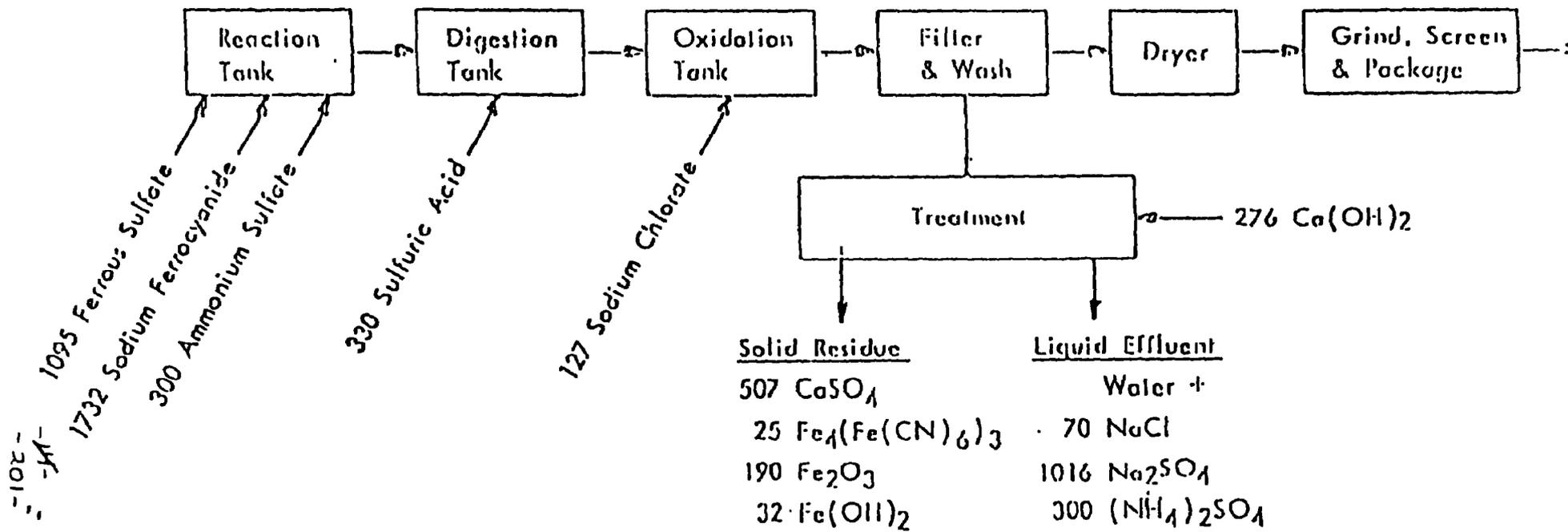
#### G. Manufacture of Iron Blue Pigments

Iron blue pigments are produced by the reaction of sodium ferrocyanide with an aqueous solution of iron sulfate and ammonium sulfate. The precipitate formed is separated and oxidized with sodium chlorate or sodium chromate, a hexavalent chromium compound, to form iron blues ( $\text{Fe}(\text{NH}_4[\text{Fe}(\text{CN})_6])$ ). The product is filtered, dried and packaged as shown in Figure 7. The filtrate, containing ferric ferrocyanide (and hexavalent chromium when sodium chromate is used as an oxidizing agent) is sent to wastewater treatment.

#### Waste Generation and Composition

Some plants produce different pigments in sequence, while others manufacture several pigments concurrently and combine the wastewaters for treatment at a single facility. The wastewaters contain unreacted materials, by-products of reaction, and unprecipitated pigment products. Wastewater treatment generally involves reduction of metal ions (such as chrome VI) if necessary, neutralization, and precipitation of metals with lime or caustic soda.

The efficiency of the removal of hexavalent chromium depends on the extent of its reduction. If reduction is incomplete, and if neutralization and metal precipitation take place too rapidly, hexavalent chromium is likely to be entrained in the precipitating sludges, resulting in their contamination with hexavalent chromium. The higher the concentration of hexavalent chrome in the wastewater, the greater



(3)  
FIGURE 7 IRON BLUE MANUFACTURE

is the likelihood of its inefficient or ineffective reduction, and the consequent likelihood of the contamination of chromium hydroxide sludges with hexavalent chrome. Screening and verification data from three chrome pigment plants show appreciable concentrations of chromium in raw waste streams: (55-310 ppm), presumably in hexavalent form.(1) At one facility treated waste effluent contained 130 ppm of chromium.(1)

The composition of the wastewater treatment sludge from chromium pigments production is dependent upon the pigments which are being manufactured, as shown in Table 1 below, and whether wastes from multi-process plants are combined for treatment. With regard to the waste constituents of regulatory concern, chromium is usually present and lead may also be found. Ferric ferrocyanide is a component of the sludge when iron blues are produced. Table 1 lists the chromium, lead and cyanide-containing compounds in the respective sludges, and their amounts relative to the amount of the sludges.

The Agency lacks data on the precise total amounts of hazardous constituents in the sludges. These amounts, however, are believed to be substantial. Data indicates that wastewaters from all chromium pigment plants accumulate 8,450 lbs. of chromium, 2,538 lbs of lead and 157 lbs of cyanide per day (2). Because treatment of the wastewaters is effected by consolidation of contaminants in the sludge, the sludge is expected to contain much higher concentrations of

those contaminants. Moreover, as shown by the material balances indicated on Figures 1-7 above, and the data of Table 1, compounds of hexavalent chromium and lead are significant constituents of the treatment sludges, and are estimated to be present in substantial concentrations.

Except for the production of chromic oxide pigments, and the production of iron blue pigments if sodium chromate is not used, the untreated wastewater from chromate pigment production contain chromium in the hexavalent form (see Table I), the manufacture of these different products typically occurs either in alternating or simultaneous mode at the same production facility. Thus, even though some individual product lines may not result in wastes containing hexavalent chrome, the sludges in toto are expected to be contaminated.

The remaining listed hazardous waste, oven residue from the production of hydrated chrome oxide green pigments, is generated when sodium dichromate and boric acid are heated to form the pigment product. A chromium containing compound (probably containing unreacted hexavalent chrome)<sup>(8)</sup> is found in the oven residue as a result of chromium in the feed material.

The amount of sludge generated is quite substantial. The Agency estimates that approximately 2,100 to 2,600 metric tons of sludge are currently generated per year by treatment of wastewaters from the manufacture of chromium pigments.<sup>(4)</sup> The amount of wastewater treatment sludge is expected to increase significantly in the near future. Treatment standards

based on Best Practicable Technology (BPT) are being developed for the chromium pigments industry, and compliance will result in removal of at least 95% of the chromium and lead from wastewaters. Using current production figures, the Agency estimates that about 4300 metric tons per year (dry weight) of sludge will be generated by the industry when BPT standards are implemented.(1)

The Agency emphasizes, however, that the amounts of the hazardous constituents lead and hexavalent chromium in these sludges appear to be sufficiently high to be of regulatory significance.

#### Current Waste Management Practice

A report by the Versar Corporation in 1975 indicates that, at that time, eight companies manufacturing chromium pigments disposed of their wastewater treatment sludge on land.(3) Two companies disposed on-site, one by ponding and the other using landfill after treatment. Six companies disposed off-site, one to a municipal landfill, one to a land dump and four to private landfills. Another company discharged to the sewer and one claimed to recover its wastes.(3)

#### Hazards Posed by These Wastes

These wastes may pose a substantial threat to human health and the environment if the hazardous constituents are released to the environment, and environmental release may occur as a result of waste mismanagement. In the sludges, lead and chromium occur as pigment particles, as hydroxides,

and presumably, as entrained hexavalent chromium; these compounds may be solubilized if the wastewater treatment sludges are improperly managed. (See Attachment I to this document.) Solubilization of lead is pH-dependent, and increases as the pH of the solubilizing medium decreases.(3) If the sludges are exposed to acidic conditions (which might occur due to co-disposal with waste acids, or in municipal landfills or in areas where acid rain is prevalent), this toxic metal could be released from the waste matrix. Furthermore, lead hydroxide if present in sufficient quantities, is soluble enough in water to exceed the National Interim Primary Drinking Water Standard (NIPDWS) of 0.05 mg/l.(5)

Most hexavalent chromium compounds, both chromates and dichromates have very high water solubility. Therefore hexavalent chrome, if present in these wastes, will leach into groundwaters and effluent streams, and is likely to pollute such waters in amounts significantly exceeding the NIPDWS of 0.05 mg/l.

Water is likely to come into contact with the waste in several ways. Open dumping or improper management of a landfill may permit percolation of rainwater through the waste pile or allow surface run-off to solubilize hazardous constituents. Placement of the waste below the water table could result in leaching of the lead (and possibly chromium) by groundwater. Clearly, wastes that require ponding are in contact with a substantial amount of liquid, which could

encourage leaching or form a head, facilitating leachate migration to groundwater. If control practices are nonexistent or inadequate, contaminant-bearing leachate, run-off or impoundment overflow may reach ground and surface waters, polluting valuable water supplies for a considerable period of time.

Wastewater treatment sludges from iron blues production may release cyanides to air or groundwater and thus also create a substantial hazard if improperly managed. Ferric ferrocyanide itself has little migratory potential. It is insoluble in water and has been observed to be quite immobile in soil column studies (Appendix A). Ferrocyanides, however, undergo decomposition upon exposure to sunlight, releasing cyanide and hydrogen cyanide gas. Once released from the matrix of the waste, hydrogen cyanide gas will volatilize and enter the atmosphere. Cyanide, once released, appears to be fairly mobile in soils (Appendix A). Even clay liners beneath a disposal site might not impede cyanide migration significantly; in the presence of water, montmorillonite clays sorbed cyanide weakly (6). Cyanide thus is capable of migrating from the waste disposal site to ground and surface waters.

Since lead is an element, it does not decompose, and will not degrade with the passage of time. If it escapes from the disposal site, it will continue to provide a potential source of long-term contamination. Lead is bio-

accumulated and passed along the food chain but is not biomagnified.

The Agency has determined to list chromium pigments and iron blues as T hazardous wastes on the basis of lead, hexavalent chromium, and ferrocyanide constituents (for iron blues), although two of these constituents are also measurable by the EP extraction procedure toxicity characteristic. There are other factors (in addition to those measured by the EP toxicity characteristic) which justify the T listing. Some of these factors already have been identified, namely the non-degradability of these substances, indications of lack of proper management of the wastes in actual practice and the presence of ferrocyanide as a waste constituent in iron blues. The quantity of these wastes generated is an additional supporting factor.

As indicated above, wastes from the production of chromium pigments and iron blues are generated in very substantial quantities and the amounts generated are expected to increase. Each waste contains substantial amounts of lead, chromium, or ferrocyanides, and several wastes contain more than one of these contaminants. Most of the chromium in the sludge will be in the trivalent form, but, as explained above, it is expected that regulatorily significant concentrations of hexavalent chromium will remain. Large amounts of each of these contaminants are thus available for potential environmental release, posing the danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time, since large amounts of pollutants are available for environmental loading. Attenuative

capacity of the environment surrounding the disposal facility could also be reduced or exhausted by large quantities of pollutants released from the waste.

All of these considerations increase the possibility of exposure to the harmful constituents in the wastes, and in the Agency's view, support a T listing.

#### Adverse Health Effects of Constituents of Concern

Ingestion of drinking water from ground and surface waters contaminated by lead and hexavalent chromium threatens human health. Aquatic species exposed to the heavy metals may also be adversely effected.

Carcinogenicity of various hexavalent chromium compounds in humans is well documented, (18) and EPA's CAG has determined that there is substantial evidence that hexavalent chromium compounds are carcinogenic to man. In one study rats showed a weak carcinogenic response to trivalent chromium compounds. Oral administration of trivalent chromium results in little chromium absorption. The degree of absorption is slightly higher following administration of hexavalent compounds. Chronic toxicity problems associated with chromium include damage to liver, kidney, skin, respiratory passages and lungs. Allergic dermatitis can result from exposure to both tri- and hexavalent chromium.

No data for chronic toxicity of trivalent chromium for freshwater fish or algae are available. The chronic toxicity

value for the freshwater invertebrate Daphnia magna; based on a single study, is reported as 445 mg/l. (CRIII) and 10 ug/l (CrVI). Chronic embryo-larval tests on six species of freshwater fish exposed to Cr VI resulted in values ranging from 37 to 72 ug/l.

Ferrocyanides exhibit low toxicity, but release cyanide ions and toxic hydrogen cyanide gas upon exposure to sunlight. Cyanide compounds can adversely affect a wide variety of organisms because of their inhibition of respiratory metabolism. Appendix A contains a more detailed discussion of the adverse health and environmental effects of chromium and of cyanide.

The hazards associated with lead, chromium, and cyanide-containing compounds have been recognized by other regulatory programs. Lead and chromium are listed as priority pollutants in accordance with §307 of the Clean Water Act, and National Interim Primary Drinking Water Standards (NIPDWS) have been established pursuant to the Safe Drinking Water Act.

The ambient water quality criterion for hexavalent chromium is recommended to be identical to the existing NIPDWS for total chromium, which is 50 ug/l. For total recoverable hexavalent chromium the criterion to protect freshwater aquatic life is 0.29 ug/l (24 hour average), not to exceed 21 ug/l at any time. To protect saltwater aquatic life the corresponding concentrations are 18 ug/l and 1260 ug/l.

The OSHA time-weighted average exposure criterion for chromium (carcinogenic compounds) is 1 ug/m<sup>3</sup>; for the "non-carcinogenic" class of chromium compounds the criterion is 25 ug/m<sup>3</sup>.(19)

## Attachment I

### SOLUBILITY AND ENVIRONMENTAL MOBILITY

### CHARACTERISTICS OF CHROMIUM COMPOUNDS

The tripositive state is the most stable form of chromium. In this state chromium forms strong complexes (coordination compounds) with a great variety of ligands such as water, ammonia, urea, halides, sulfates, amines and organic acids.(10,11) Thousands of such compounds exist. This complex formation underlies the tanning reactions of chromium, and is responsible for the strong binding of trivalent chromium by soil elements, particularly clays.(13,15)

At pH values greater than about 6, trivalent chromium forms high molecular weight, insoluble, "polynuclear" complexes of  $\text{Cr}(\text{OH})_3$  which ultimately precipitate as  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . This process is favored by heat, increased chromium concentration, salinity and time.(10) These chromium hydroxy complexes, formed during alkaline precipitation treatment of Cr-bearing wastes, are very stable, and relatively unreactive, because the water molecules are very tightly bound. In this form Cr is therefore resistant to oxidation. Three acid or base catalyzed reactions are responsible for the solubilization of chromium hydroxide:

Cr III concentration calculated from  
Keq (mg/l).

<u>Reaction</u>	<u>Keq</u> (18)	<u>Concentration (mg/l)</u>		
		<u>pH5</u>	<u>pH6</u>	<u>pH7</u>
1. $\text{Cr(OH)}_3 + 2\text{H}^+ \rightleftharpoons \text{CrOH}^{++} + 2\text{H}_2\text{O}$	$10^8$	520	5.2	0.052
2. $\text{Cr(OH)}_3 \rightleftharpoons \text{Cr}^{+3} + 3\text{OH}^-$	$6.7 \times 10^{-31}$	35	0.035	1*
3. $\text{Cr(OH)}_3 \rightleftharpoons \text{H}^+ + \text{CrO}_2^- + \text{H}_2\text{O}$	$9 \times 10^{-19}$	1	1	1

\*1=<0.001 mg/l

It is apparent from these figures that, in theory, trivalent chromium could leach from sludges to some extent. Such solubilized chromium, however, is unlikely to contaminate aquifers. It is complexed with soil materials, and tenaciously held.(10,15) Little soluble chromium is found in soils.(10,12) If soluble trivalent chromium is added to soils it rapidly disappears from solution and is transformed into a form that is not extracted by ammonium acetate or complexing agents.(12,13) However, it is extractable by very strong acids, indicating the formation of soluble hydroxides.(13,15) Thus: above pH 5, chromium (III) is immobile because of precipitation; below pH 4 chromium (III) is immobile because it is strongly adsorbed by soil elements; between pH 4 and 5 the combination of adsorption and precipitation should render trivalent chromium

quite immobile.(13,15)

In contrast, hexavalent chromium compounds are quite soluble, and hexavalent chromium is not as strongly bound to soils.(13,15) Hexavalent chromium remains as such in a soluble form in soil for a short time, and is eventually reduced by reducing agents if they are present.(12,14) As compared with the trivalent form, hexavalent chromium is less strongly adsorbed and more readily leached from soils,(15) and thus is expected to have high mobility in soil materials.(15)

### References

1. US EPA, Effluent Guidelines Division. Draft Development Document for Inorganic Chemicals Manufacturing Point Source Category. (Proposed). June 1980; EPA 440-11-79/007.
2. US EPA Effluent Guidelines Division. Inorganic Chemicals BAT Review. EEM/DH. May 1979
3. US EPA, Office of Solid Waste. Assessment of Industrial Hazardous Waste Practices Inorganic Chemicals Industry. US EPA Contract No. 68-01-2246. March 1975. NTIS PB-244-832.
4. Undated memorandum from C. Dysinger to V. Steiner on Chromium pigments and iron blues document.
5. Handbook of Chemistry and Physics, 48th Ed. The Chemical Rubber Company. 1967-68.
6. Cruz, M., et al. 1974. Absorption and Transformation of HCN on the Surface of Copper and Calcium Montmorillonite. Clay Minerals 22:417-425.
7. US EPA Open files. Hazardous Site Control Branch, WH-548, US EPA, 401 M Street, S.W., Washington, D.C. 20460. Contact Hugh Kaufman (202)755-3051.
8. Latimer, W. M. and J. H. Hildebrand. 1940. Reference Book of Inorganic Chemistry. MacMillan, New York.
9. Laboratory Waste Disposal Manual. Manufacturing Chemists Association, Washington, D.C., 1970.
10. U.S. EPA, Review of the Environmental Effects of Pollutants; III Chromium. ORNL/EIS-80; EPA-600/1-78-023; May 1980.
11. Transition Metal Chemistry, R. L. Carlin, ed. Marcel Dekker, New York. 1965; Volume 1.
12. U.S. EPA. Application of Sewage Sludge to Cropland; Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals. EPA 430/9-76-013. NTIS PB No. 264-015. November, 1976.
13. Bartlett, R. J. and J. M. Kimble. Behavior of Chromium in Soils: I Trivalent Forms. J. Environ. Qual. 5: 379-383: 1976.

14. Bartlett, R. J. and J. M. Kimble. Behavior of Chromium in Soils: II Hexavalent Forms. *Ibid.* 5:383-386. 1976.
15. Griffin, R. A., A.K. Au, and R. R. Frost. Effect of pH on adsorption of chromium from landfill leachate by clay minerals. J. Environ. Sci. Health A12(8): 430-449:1977.
16. National Academy of Sciences. Medical and Biological Effects of Environmental Pollutants; Chromium. Washington, D.C. 1974.
17. U.S. EPA. Treatability studies for the Inorganic Chemicals Manufacturing Point Source Category. EPA-440/1-80/103.
18. U.S. EPA. Chromium; Ambient Water Quality Criteria EPA 440/5-80-035, October 1980.
19. 29 CFR 1910.1000
20. Cassarett, L. J. and J. Doull, 1979. Toxicology, the Basic Science of Poisons, Second edition. MacMillan, New York.

## **Organic Chemicals**

## LISTING BACKGROUND DOCUMENT

## ACETALDEHYDE PRODUCTION

Distillation bottoms from the production of acetaldehyde from ethylene (T)

Distillation side cuts from the production of acetaldehyde from ethylene (T)

I. Summary of Basis for Listing

Distillation bottoms and distillation side cuts from acetaldehyde production from ethylene contain suspected carcinogens such as chloroform, and formaldehyde and contain other toxic materials as well.

The Administrator has determined that the still bottoms from acetaldehyde production from ethylene may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. The wastes contain chloroform and formaldehyde which have been identified by the Agency as exhibiting substantial evidence of carcinogenicity, as well as other toxic materials, including methylene chloride, methyl chloride, paraldehyde, and formic acid.
2. The wastes are held in settling ponds prior to deep well injection or they are disposed of in lagoons. While in the settling ponds and lagoons, there is the potential for ground and surface water contamination by leaching and flooding. Additionally, there is risk of volatilization of the toxic waste components from the settling ponds and human exposure via inhalation.
3. The wastes are persistent in the environment and tend to bioaccumulate so that there is a potential for widespread exposure through volatilization or drinking water contamination.

## II. Source of the Waste and Typical Disposal Practices

### A. Profile of the Industry

Acetaldehyde ( $\text{CH}_3\text{CHO}$ ) is a high-volume production chemical intermediate used principally in the manufacture of acetic anhydride, butyraldehyde, chloral, pyridines, and other chemical derivatives. Most acetaldehyde is manufactured by the liquid-phase oxidation of ethylene.<sup>(1)</sup> Acetaldehyde is produced in three plants in the U.S., which utilize ethylene for starting material.<sup>(2)</sup>

Table 1 provides a list of the ethylene-based plants, their locations, and their production capacities.

TABLE 1

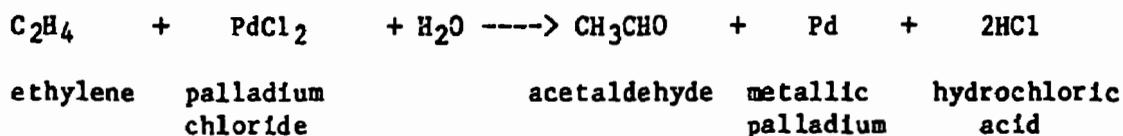
Acetaldehyde Producer Locations, Annual Production Capacities and Raw Materials Used (2)(4)

<u>Company</u>	<u>Facility</u>	<u>1978 Production Capacity (Gg/Yr) (metric tons/yr x 10<sup>3</sup>)</u>	<u>Raw Material</u>
Celanese Corp.			
Celanese Chem. Co. Div.	Bay City, Tx. Clear Lake, Tx.	136 277	Ethylene Ethylene
Eastman Kodak Co.			
Eastman Chemical Products, Inc., subsidi. Texas			
Eastman Co.	Longview, Tx.	277	Ethylene (90%); ethyl alcohol (10%)
Total		690	

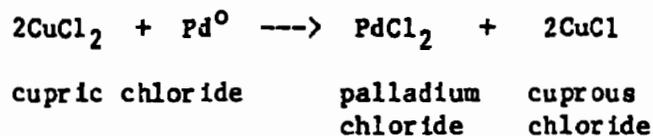
## B. Manufacturing Process

The direct liquid-phase oxidation of ethylene is the most widely used method for the manufacture of acetaldehyde. Ethylene is catalytically oxidized with air in a dilute hydrochloric acid solution containing the chlorides of palladium and copper.(3,4,5)

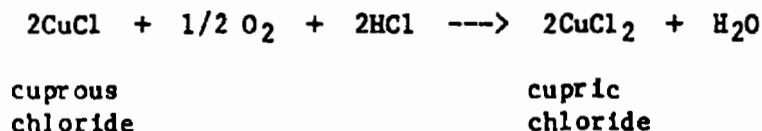
The process involves the oxidation of ethylene by palladium chloride to form product acetaldehyde, palladium metal and hydrogen chloride:



Cupric chloride is used as the second component of the catalyst system to reoxidize the palladium metal to palladium chloride:



The cuprous chloride thus formed is, in turn, reoxidized in the second stage regeneration unit to cupric chloride:



C. Waste Generation, Waste Composition and Waste Management

1. Waste Generation and Composition (3,4,5)

The process which generates the subject waste is shown in Figure 1. Ethylene feed gas goes to a tubular reactor where it mixes with palladium chloride and copper chloride in solution at 9 atmospheres of pressure and a temperature of 130°C. The reaction products are flash evaporated and the product acetaldehyde passes overhead to the crude distillation column. The aqueous bottoms go to a reactor where the palladium catalyst is regenerated and recycled to the acetaldehyde reactor. The overhead from the crude distillation column is condensed; unreacted ethylene and light hydrocarbons (including a small amount of acetaldehyde) are vented. The crude acetaldehyde from the bottom of this column then goes to final distillation. Purified acetaldehyde is distilled overhead. Two wastes are obtained: the side-cuts and the bottoms. The distillation bottoms (discharge wastewater) containing high-boiling organic impurities leaves the still at the bottom; and the side-cut stream consists of higher boiling organic and chlorinated organics is removed as a side stream higher up the column. (4,7)

Table 2 shows the analytical composition of waste discharges for the two streams.

Table 3 presents data on 1978 acetaldehyde production capacity, estimated production, and estimated generation of still bottom and side cut wastes for the three plants which produce acetaldehyde by direct liquid-phase oxidation of ethylene.

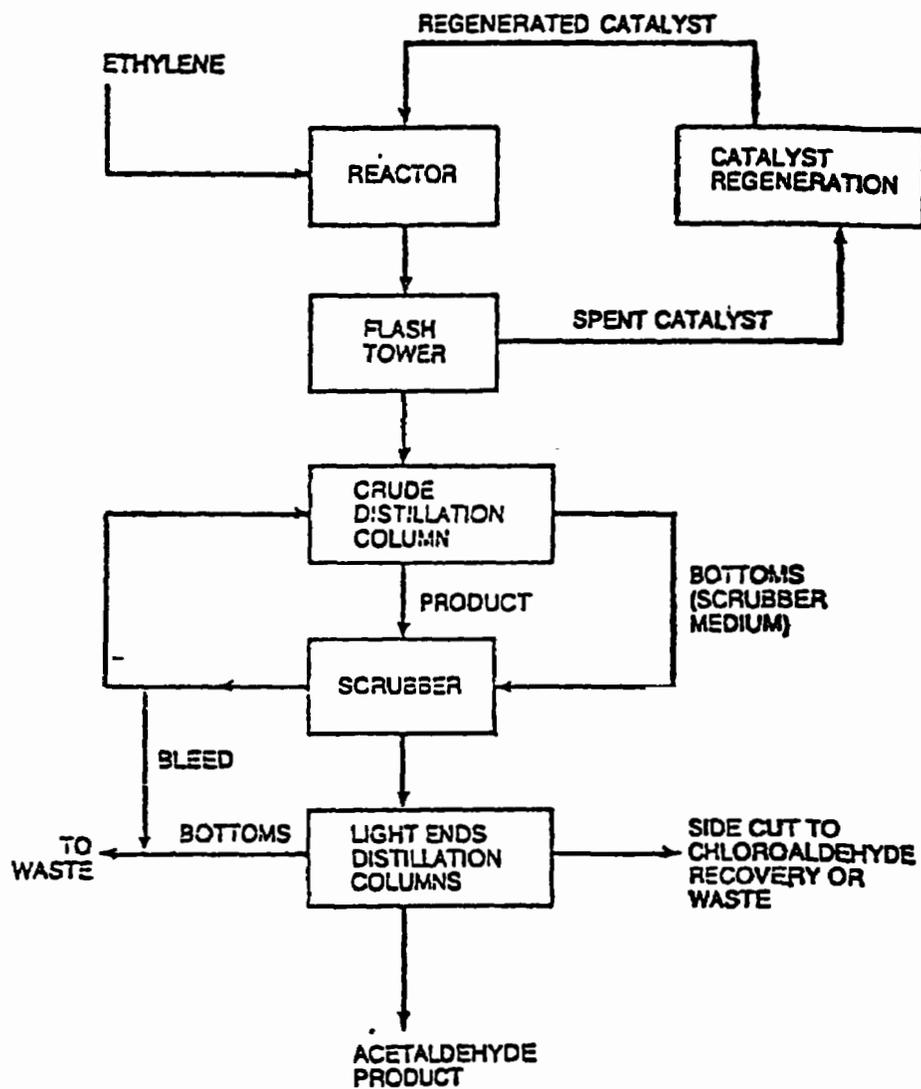


Figure 1. SIMPLIFIED ACETALDEHYDE SCHEMATIC PROCESS FLOW

TABLE 2

Uncontrolled Waste Discharge Ratio (4)  
(g of discharge per kg of acetaldehyde)

Component	Formula	Distillation Bottoms (Discharge Wastewater)	Distillation Side-Cut	Combined *>
Ethylene	C <sub>2</sub> H <sub>4</sub>	-	-	-
Acetaldehyde	C <sub>2</sub> H <sub>4</sub> O	-	7.8	7.8
Acetic Acid	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>	13.9	0.6	14.5
Chloroacetaldehyde	C <sub>2</sub> H <sub>3</sub> OC1	-	5.5	5.5
Acetyl chloride	C <sub>2</sub> H <sub>3</sub> OC1	4.2	5.0	9.2
Chloral	C <sub>2</sub> HOC1 <sub>3</sub>	2.1	3.4	5.5
Paraldehyde	(C <sub>2</sub> H <sub>4</sub> O) <sub>3</sub>	1.6	-	1.6
Other organics (including chloro- form, formaldehyde and methylene and methyl chloride)		4.0	2.0	6.0
TOTAL Volatile Organics:		25.8	24.3	50.1
Water	H <sub>2</sub> O	795.6	25.5	821.1
TOTAL STREAM:		821.4	49.8	871.2

\*>These totals are combined because combination of the two waste streams is a known method disposal. (4)

Table 3  
Estimated Still Bottom Generation from Acetaldehyde Production - 1978<sup>a</sup>

<u>Company</u>	<u>Location</u>	<u>1978 Production Capacity (1000 MT/yr)</u>	<u>Estimated Production<sup>b</sup> (1000 Mt/yr)</u>	<u>Estimated Still-Bottom Wastewater Generated (1000 Mt/yr)</u>	<u>Estimated Side-Cut Waste Generated<sup>c</sup> (1000 Mt/yr)</u>	<u>Total (1000 Mt)</u>
Celanese Chemical	Bay City, TX	136	97	111	5	116
Celanese Chemical	Clear Lake City, TX	277	197	227	10	237
Texas Eastman	Longview, TX	<u>277</u>	<u>197</u>	<u>227</u>	<u>10</u>	<u>237</u>
TOTAL:		690	491	565	25	590

<sup>a</sup>Based on data from reference 4.

<sup>b</sup>Based on 1976 industry average of 71% production, 1000 MT/yr.

<sup>c</sup>Based on Figures in Table 2, 1000 MT/yr.

## 2. Waste Management

Reported disposal of the side cuts has been by deep well injection.<sup>(4)</sup> Wastewater from the distillation bottoms has been disposed of both by deep well injection and in anaerobic lagoons.<sup>(4)</sup> One of the three domestic plants producing acetaldehyde from ethylene disposes of both side cuts and wastewater by deep well injection.<sup>(4)</sup> This plant combines the two wastes prior to injection.<sup>(4)</sup> Deep well injection requires waste presettling and flow equalization via ponding prior to injection to avoid well obstruction. So that the wastes from this plant are also managed at least for a time in holding ponds.

The waste constituents of concern are chloroacetaldehyde, paraldehyde, chloroform, formaldehyde, methylene chloride, methyl chloride and formic acid. Acetyl chloride and chloral, although dangerous, are expected to hydrolyse rapidly upon aqueous disposal, so that there is little possibility of migration and exposure (App. B.) (42).

### III. Discussion of Basis for Listing

#### A. Hazards Posed by the Waste

The toxic components present in these wastes include the compounds listed below in Table 4.

Table 4. Toxic Components in the Waste

- |                      |                      |
|----------------------|----------------------|
| o Chloroform         | o Paraldehyde        |
| o Formaldehyde       | o Formic acid        |
| o Methylene chloride | o Chloroacetaldehyde |
| o Methyl chloride    |                      |

A number of these compounds are known or suspected carcinogens or mutagens while all exhibit toxic properties.

These waste constituents are capable of migration by leaching or by volatilization from lagoons or holding ponds (the management method for both waste streams, see p. 8 above), and of reaching environmental receptors should the wastes be improperly managed.

As to the migratory potential of waste constituents, chloroacetaldehyde, which is present in high concentrations (4), is highly soluble (App. B.). Although subject to degradation, the most significant degradation mechanism for chloroacetaldehyde is biodegradation, and thus chloroacetaldehyde would be expected to persist for long periods in the abiotic conditions of an aquifer. (42) Further, chloroacetaldehyde is highly volatile (vapor pressure 100 mm Hg), and thus could migrate via an air exposure pathway. (42) Chloroacetaldehyde is in fact an extremely noxious vapor, with a TLV of 1 ppm.

(42) Thus, this threshold could be exceeded in areas in the vicinity of the lagoon if chloroacetaldehyde were to volatilize at rates four levels of magnitude less than its actual volatility potential. (42)

Paraldehyde, another waste constituent present in high concentrations (4), is capable of migrating via ground or surface water, since it is extremely soluble (120,000 ppm). (42) Bacterial degradation is the chief degradation mechanism (42), so this compound would likely persist in an abiotic environment such as that of most groundwaters.

Other contaminants of concern are likewise capable of migrating and persisting via water or air exposure pathways. Chloroform, for example is highly soluble (8200 ppm). Although it adsorbs to organic soil constituents and to clay surfaces, management could occur in areas with highly permeable soil or soils low in organic content, so that mobility would not be significantly impeded. Chloroform hydrolyses slowly, and so could persist for substantial periods in ground and surface waters (half life of 18 months in dark water). (42)

Thus, virtually all chloroform emitted from a lagoon is expected to persist in groundwater or reach surface waters via groundwater movement (App. B.). Such behavior is likely to result in exposure to humans using such groundwater sources as drinking water supplies within adjacent areas. Such movement and persistence of chloroform has been observed.(17) Chloroform has been detected in groundwater supplies in Miami, Florida.(18)

Movement of chloroform within surface water is likely to result in exposure to aquatic life forms in rivers, ponds, and reservoirs (App.B.). Similarly, potential exposure to humans is likely where water supplies are drawn from surface waters.

Chloroform is projected to be released to the atmosphere from surface water systems (App. B.). Although chloroform decomposes slowly in air when it is exposed to sunlight, the photochemical degradation products are carbon tetrachloride, a carcinogen, (47) and phosgene, a highly toxic gas. In addition, photochemical degradation mechanisms result in chlorine burden. At stratospheric levels, atomic chlorine reduces the levels of ozone which shields the earth from harmful radiation.(20)

Formaldehyde is also capable of migrating and reaching environmental receptors via a groundwater exposure pathway since it is miscible. Biodegradation is the most significant degradation mechanism, so that formaldehyde would be likely to persist in groundwater. (33) Formaldehyde also oxidizes to form toxic formic acid, increasing the likelihood of exposure to that substance. (33)>

Formic acid could itself migrate via both an air and water pathway, being both highly volatile and miscible. (33) Formic acid would have high mobility so long as soils were not basic and were low in organic content. (33)

Both methylene chloride and methyl chloride also are capable of migrating and persisting via air and water exposure pathways, as both waste constituents are quite soluble (although methylene chloride is significantly more soluble than methyl chloride), and also highly volatile (33).

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>Soil attenuation would not significantly impede formaldehyde's migratory potential in areas where soil is highly permeable or low in organic constituents (33).

Virtually all of the methylene chloride and methyl chloride discharged from a lagoon is expected to persist in groundwater or reach surface waters via groundwater movement (App. B.). Such behavior is likely to result in exposure to humans who use such groundwater sources as drinking water supplies within adjacent areas.

Both methylene chloride and methyl chloride are likely to be released to the atmosphere from surface water systems (App. B.). Furthermore, there may be high local concentrations of these compounds near disposal sites due to their high volatility which could also result in serious adverse effects to individuals residing near such sites, due to exposure to high vapor concentrations.

The persistence of many of the contaminants of concern has been demonstrated through analysis of leachates from actual disposal sites. Chloroform has been found in PPM concentrations at Love Canal, while methyl chloride levels reached 180 ppb. (43,44,45) Leachate from the Story chemical site included methylene chloride in the ppm range. (46)

As demonstrated above, therefore, the waste constituents of concern are capable of migrating and persisting if these wastes are managed improperly. Improper management is certainly reasonably plausible or possible. Thus, lagoons or holding ponds may be sited in areas with highly permeable soils, and may lack adequate leachate control features. There may be inadequate cover to impede migration of volatile waste constituents. There may also be inadequate flood control measures to impede waste washout in the event of heavy rainfall. Thus, mismanagement could realistically occur, resulting in substantial hazard.

The Agency is aware that most of the waste constituents of concern (with the exception of chloroacetaldehyde and paraldehyde) are likely to be present in small concentrations. In light of the high potential for substantial hazard associated with these materials, the concentrations are deemed sufficient to warrant regulation as hazardous. The Agency's policy for carcinogens in water, for example, is that any exposure to a carcinogen will induce an oncogenic response in a human receptor, and that the greater the concentration of the carcinogenic substance, the greater the likelihood of response. (See 44 FR 15926, 15940 (March 15, 1979)). In light of the carcinogenic potential of many of these waste constituents, therefore, even small (<100 ppm) concentrations are considered significant.

Furthermore, the wastes are generated in significant quantities (see Table 3 above) so that large amounts of all waste constituents are available for environmental release, increasing the likelihood of exposure. There is also more chance of a major damage incident should wastes be mismanaged. The quantity of waste generated is thus a further reason supporting the hazardous waste listing of these two waste streams from production of acetaldehyde.

## B. Health and Ecological Effects

### 1. Chloroform

Health Effects - Designated a priority pollutant by U.S.E.P.A., chloroform has been judged as having high carcinogenic potential in humans on the basis of substantial evidence of its carcinogenicity. (10,11,47) Chloroform also is considered a toxic chemical [oral rat LD<sub>50</sub>= 800 mg/Kg].

Other studies have demonstrated that chloroform can cause a variety of teratological and other effects in animals, such as missing ribs, delayed skull ossification, maternal toxicity, and fetotoxicity, when it is administered orally or in a vapor phase. (12,13) Occupational exposure situations have resulted in damage to liver and kidneys with some signs of neurological disorder. (14) Manifestation of the toxic nature of chloroform is, in part, attributable to the observation that metabolism results in toxication rather than detoxication. (15,16) Additional information and specific references on the adverse effects of chloroform can be found in Appendix A.

Ecological Effects - Chloroform has been found to be acutely toxic at high concentrations to bluegill and rainbow trout.

Industrial Recognition of Hazard - Chloroform has been given a moderately toxic hazard rating via oral and inhalation routes by Sax in Dangerous Properties of Industrial Materials.

Regulations - OSHA has set the TWA at 50 ppm.

## 2. Methylene chloride and methyl chloride

Health Effects - Methylene chloride<sup>(21)</sup> and methyl chloride are mutagenic. (22,23) Methylene chloride was also reported to be fetotoxic or embryo-toxic to rats and mice. (48)

Exposures to high vapor concentrations of methylene chloride can produce dizziness, nausea and numbness of the extremities; (24) prolonged exposure to concentrations near 500 ppm could result in central nervous system depression and elevated levels of carboxyhemoglobin,

levels that reduce the blood's ability to carry oxygen and thus cause asphyxiation. Similar toxicological effects are expected with exposure to methyl chloride. Severe contamination of food or water can result in irreversible renal and hepatic injury.(25)

Exposure to high concentration can cause death.(26) Additional information and specific references on the adverse effects of methylene chloride and methyl chloride can be found in Appendix A.

Ecological Effects - In laboratory tests, high concentrations of methyl chloride are acutely (96-hours) toxic to aquatic organisms, e.g., the bluegill.(27) Similarly, methylene chloride also is actively toxic.(28,29)

Regulations - The OSHA standard adopted for methylene chloride is TWA 500 ppm. The OSHA standard for methyl chloride is 100 ppm.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, designates methylene chloride as highly toxic via inhalation and moderately toxic via oral and skin routes. Methyl chloride is designated highly toxic via inhalation.

### 3. Formaldehyde

Health Effects - Formaldehyde has been reported to be carcinogenic,(30,31) mutagenic(32) and teratogenic.(33) The Agency has also identified formaldehyde as a compound which exhibits substantial evidence of being carcinogenic. It is toxic [oral rat LD<sub>50</sub> = 600 mg/Kg] causing inflammatory effects in many mammalian species.(34) Additional information and specific references on the adverse effects of formaldehyde can be found in Appendix A.

Ecological Effects - Formalin, an aqueous solution of formaldehyde, can cause toxic effects to exposed aquatic life.(35) It is lethal to Daphnia magna.(36)

Regulations - OSHA has set a standard air TWA limit of 3 ppm for formaldehyde.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, lists formaldehyde as highly toxic to skin, eyes and mucous membranes.

#### 4. Chloroacetaldehyde

Health Effects - Chloroacetaldehyde is a toxic chemical which is mutagenic and a proposed carcinogen.(37,38,39) It is extremely corrosive upon contact and can cause severe effects to the skin, eyes, and respiratory tract. Upon decomposition, conversion to methyl chloride takes place and, as previously discussed, methyl chloride is a known mutagen. Additional information and specific references on the adverse effects of chloroacetaldehyde can be found in Appendix A.

Regulations - The OSHA standard for chloroacetaldehyde is 1 ppm in air.

Industrial Recognition of Hazard - Chloroacetaldehyde is designated as a highly toxic irritant in Sax, Dangerous Properties of Industrial Materials.

5. Paraldehyde

Health Effects - Paraldehyde is a toxic chemical [oral rat LD<sub>50</sub> = 1530 mg/Kg]. It has been implicated in human fatalities in which congestion of the lungs and dilation of the right side of the heart occurred following oral ingestion of the chemical.(41)  
Additional information and specific references on the adverse effects of paraldehyde can be found in Appendix A.

6. Formic Acid

Health Effects - Formic acid is toxic [oral rat LD<sub>50</sub> = 1,210 mg/Kg] and ingestion of even small amounts for short periods may cause permanent injury or severe damage to skin, eyes, and mucosal membranes. Because it is rapidly absorbed through the lungs, chronic exposure to formic acid vapors can result in blood in urine. The OSHA (1976) and ACGIH (1977) standards for the workplace are 5 ppm. Additional information and specific references on the adverse effects of formic acid can be found in Appendix A.

Regulations - The OSHA standard for formic acid is a TWA of 5 ppm.

Industrial Recognition of Hazard - Formic acid is designated as highly toxic via ingestion, moderately toxic via inhalation and moderately toxic as a skin irritant in Sax, Dangerous Properties of Industrial Materials.

#### IV. References

1. Hayes, E.R. Acetaldehyde. Kirk-Othmer encyclopedia of chemical technology. 2nd ed. V.I. Interscience Publishers, New York. pp.77-95. 1963.
2. Stanford Research Institute. 1978 Directory of chemical producers - U.S.A. SRI International. Menlo Park, California. pp. 1127. 1978.
3. Kirk-Othmer Encyclopedia of Chemical Technology. 2nd ed. V.I. John Wiley and Sons, Inc., New York. pp. 86, 87. 1970.
4. Lovell, R.J. Acetaldehyde product report. Emissions control options for the synthetic organic chemicals manufacturing industry (Draft). Prepared for the U.S. Environmental Protection Agency under Contract No. 68-02-2577. January, 1979.
5. U.S. EPA. Industrial process profiles for environmental use: Chapter 6. The industrial organic chemicals industry. EPA No. 600/2-77-023f. February, 1977.
6. Stanford Research Institute. 1979 Chemical economics handbook. Acetaldehyde. SRI International, Menlo Park, California. March, 1979.
7. Jira, et al. Acetaldehyde via air or oxygen. Hydrocarbon Processing, 55(3):97-100. March, 1976.
8. Not used in text.
9. Not used in text.
10. U.S. EPA. Carcinogen Assessment Group. Type II risk assessment for chloroform. 1979.
11. National Cancer Institute. Report on carcinogenesis bioassay of chloroform. NTIS PB No. 264 018. 1976.
12. Schwetz, B.A., et al. Embryo and feto-toxicity of inhaled chloroform in rats. Toxicol. Appl. Pharmacol. 28:442. 1974.
13. Thompson, D.J., et al. Teratology studies on orally administered chloroform in the rat and rabbit. Toxicol. Appl. Pharmacol. 29:348. 1974.
14. National Institute for Occupational Safety and Health. Recommended criteria for . . . occupational exposure to chloroform. No. 75-114. NTIS PB No. 246 695. 1974.
15. Ilett, K.F., et al. Chloroform toxicity in mice: Correlation of renal and hepatic necrosis with covalent binding of metabolites to tissue macromolecules. Exp. Mol. Pathol. 19:215. 1973.

References (cont.)

16. McLean, A.E.M. The effect of protein deficiency and microsomal enzyme induction by DDT and phenobarbitone on the acute toxicity of chloroform and pyrrolidine alkaloid retrosine. Brit. Jour. Exp. Pathol. 51:317. 1970.
17. RCERA Research, Inc. Priority pollutant analyses. Prepared for NUCO Chemical Waste Systems, Inc. Unpublished report. Tonawanda, NY. 1979.
18. U.S. EPA. Preliminary assessment of selected carcinogens in drinking water. EPA No. 560/4-75-003a. 1975.
19. Not used in text.
20. National Academy of Sciences, Committee on Impacts of Stratospheric change. Stratospheric ozone depletion by halocarbons: Chemistry and transport. Washington, D.C. 1979.
- 21a. Fillipova, L.M., et al. Chemical mutagens. IV Mutagenic activity of germinal system. Genetika 8:134. 1967.
- 21b. Jongen, W.M.F., et al. Mutagenic effect of dichloromethane on Salmonella typhimurium. Mutat. Res. 56:245. 1978.
22. Andrew, A.W., et al. A comparison of the mutagenic properties of vinyl chloride and methyl chloride. Mutat. Res. 40:273. 1976.
23. Simmon, V.F., et al. Mutagenic activity of chemicals identified in drinking water. S. Scott, et al., eds. In: Progress in genetic toxicology. 1977.
24. Patty, F. Industrial handbook of toxicology. Interscience Press, New York. 1979.
25. U.S. EPA. Methyl chloride: Ambient water quality criteria. NTIS PB No. 296 797. 1979.
26. MacDonald, J.D.C. Methyl chloride intoxication. Jour. Occup. Med. 6:81. 1964.
27. Dawson, et al. The acute toxicity of 47 industrial chemicals to fresh and saltwater fishes. J. Hazard. Materials 1:303. 1977.
28. U.S. EPA. In-depth studies on health and environmental impacts of selected water pollutants. Contract No. 68-01-4646. 1978.
29. Alexander, et al. Toxicity of perchloroethylene, trichloroethylene, 1,1,1-trichloroethane, and methylene chloride to fathead minnows. Bull. Environ. Contam. Toxicol. 20:344. 1978.

References (cont.)

30. Nelson, N. Letter to federal agencies: A status report on formaldehyde and HCl inhalation study in rats. New York University Medical Center, letter dated October 19, 1980.
31. Katanabe, F., et al. Study on the carcinogenicity of aldehydes; 1st report. Experimentally produced rat sarcomas by repeated infections of aqueous solutions of formaldehyde. Genn. 45:451. 1954.
32. Auerbach, C., et al. Genetic and cytogenetic effects of formaldehyde and relative compounds. Mut. Res. 39:317. 1977.
33. Humi, H., and H. Olander. Reproduction study with formaldehyde and hexamethylenetetramine in beagle dogs. Food Cosmet. Toxicol. 11:459. 1973.
34. Coon, R.S., et al. Animal inhalation studies on ammonia, ethylene glycol, formaldehyde, dimethylamine and ethanol. Tox. Appl. Pharmacol. 16:464. 1970.
35. U.S. EPA. Investigation of selected potential environmental contaminants: formaldehyde. EPA No. 560/2-76-009. 1976.
36. Dowden, B.F. and M.J. Barrett. Toxicity of selected chemicals to certain animals. Jour. Water Pollut. Control Fed. 37:1308. 1965.
37. Rannug et al. The mutagenicity of chloroethylene oxide, chloroacetaldehyde, 2-chloroethanol and chloroacetic acid, conceivable metabolites of vinyl chloride. Chem. Biol. Inter. 12(3-4):251-263. 1976.
38. Hussain and Osterman-Golkar. Comment on the mutagenic effectiveness of vinyl chloride metabolites. Chem. Biol. Interact. 12(3-4):265-267. 1976.
39. Guengerich, et al. Biochem. 18:5177-5182. 1979.
40. Waskell, L. A study of the mutagenicity of anesthetics and their metabolites. Mut. Res. 57(2):141-154. 1978.
41. Browning, E. Toxicity and metabolism of industrial solvents. Elsevier, New York. 1965.
42. Dawson, English and Petty. Physical chemical properties of hazardous waste constituents. Appendix C of the May 2, 1980 listing background document. 1980.
43. Barth, E.F., and J.M. Cohen. Evaluation of treatability of industrial landfill leachate. Unpublished report. U.S. EPA, Cincinnati, Ohio. November 30, 1978.

References (cont.)

44. O'Brien, R.P. City of Niagara Falls, N.Y. Love Canal Project. Unpublished report. Calgon Corp., Calgon Environmental Systems Div., Pittsburgh, Pa.
45. RCERA Research, Inc. Priority pollutant analyses prepared for NUCO Chemical Waste Systems, Inc. Unpublished report. Tonawanda, NY. April, 1979.
46. Sturino, E. Analytical results: Samples from store chemicals, data set others 336. Unpublished data. U.S. EPA, Region 5. Central Regional Laboratories. Chicago, Illinois. May, 1978.
47. U.S. EPA. Carcinogen Assessment Group. Office of Research and Development. List of Carcinogens. April 22, 1980.
48. Schwetz, B.A., et al. The effects of maternally inhaled trichloroethylene, perchloroethylene, methyl chloroform, and methylene chloride on embryonal and fetal development in mice and rats. Toxicol. Appl. Pharmacol. 32:84.

## LISTING BACKGROUND DOCUMENT

### ACRYLONITRILE PRODUCTION\*

Bottom stream from the wastewater stripper in the production of acrylonitrile (R,T)

Bottom stream from the acetonitrile column in the production of acrylonitrile (R,T)\*\*

Bottoms from the acetonitrile purification column in the production of acrylonitrile (T)\*\*

#### I. Summary of Basis for Listing

The hazardous wastes generated in the production of acrylonitrile contain the toxic constituents acrylonitrile, acrylamide, hydrocyanic acid, and acetonitrile. The Administrator has determined that the subject waste from acrylonitrile production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- 1) Of the constituents present in these wastes, acrylonitrile has been identified by the Agency as a substance exhibiting substantial evidence of being a carcinogen and is extremely toxic. Acrylamide is regulated as a carcinogen by OSHA. Hydrocyanic acid is extremely toxic, as is HCN gas. Acetonitrile is also toxic.

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\*In response to comments received by the Agency on the interim final list of hazardous wastes (45 FR 33123, May 19, 1980), the listing of still bottoms from final purification of acrylonitrile has been removed from the hazardous waste list (see Response to Comments at the back of this listing background document for details).

\*\*These waste streams were originally proposed in a single listing description, and are now listed separately for purposes of clarity.

- 2) The bottom streams from the wastewater stripper and the acetonitrile column, and the bottoms from the acetonitrile purification column are typically stored and settled in ponds prior to deep well disposal. If improperly stored, leachate from such systems could persist in groundwater, causing potential exposure through drinking water. Volatilization of toxic compounds from the pond also poses a risk to humans.
- 3) The bottom streams from the wastewater stripper and the acetonitrile column contain substantial concentrations of hydrocyanic acid, which can be released as hydrogen cyanide gas, an extremely toxic gas, if these wastes are exposed to mildly acidic conditions.
- 4) The aqueous wastes from this process are generated in substantial quantities, increasing the possibility of exposure should mismanagement occur.

## II. Sources of the Waste and Typical Disposal Practices

### A. Profile of the Industry

Acrylonitrile is produced in the U.S. by four producers operating six plants (Table 1). All six plants use the(SOHIO) Standard Oil of Ohio process for ammoxidation of propylene. The chemical reaction in the form of acrylonitrile may be represented by the following equation:



The reaction of propylene and ammonia results in acrylonitrile (70-80 percent), acetonitrile (3 percent), and hydrogen cyanide (HCN) (8-13 percent).(3)(4)(5) (Acetonitrile and hydrogen cyanide would

TABLE 1

## U.S. Producers of Acrylonitrile

Producer	Location	Capacity
American Cyanamid Co.	New Orleans, LA	265 MM lbs/year
E.I. duPont de Nemours & Company, Inc.	Memphis, TN	270 MM lbs/year
E.I. duPont de Nemours & Company, Inc.	Beaumont, TX	350 MM lbs/year
Monsanto Company	Chocolate Bayou, TX	440 MM lbs/year
Monsanto Company	Texas City, TX	420 MM lbs/year
Vistron Company	Lima, Ohio	<u>400 MM lbs/year</u>
		2,145 MM lbs/year

Source: Reference 2

result from the reaction of acrylonitrile and water, forming cyanohydrinacetaldehyde, which decomposes to form acetaldehyde and hydrogen cyanide. The acetaldehyde reacts with ammonia and further decomposes to form acetonitrile and water.)

By-product hydrogen cyanide is currently recovered by American Cyanamid, duPont, Monsanto, and Vistron. Acetonitrile by-product is recovered by duPont and Vistron.(3)(4)(5)

B. Manufacturing Process

A flow sheet of a typical acrylonitrile plant is shown in Figure 1. The hazardous waste streams of interest are described in Section C.

C. Waste Generation and Management

1. Bottom stream from waste water stripper in acrylonitrile production. (Stream 14, Figure 1)

Gases from the acrylonitrile reactor are cooled and neutralized in a quench column with a sulfuric acid solution. Quenched product gases then pass to the absorber where acrylonitrile, acetonitrile and hydrogen cyanide are recovered by absorption in water.

Quench column bottoms are sent to the wastewater stripper column where volatile organics are stripped with steam and recycled to the quench tower. The aqueous bottoms (Stream 14) which contain some of the catalyst, ammonium sulfate and heavy organics, are generated at the rate of about 3600 g/kg. of acrylonitrile product(7). Applying this ratio to the 1977 production figure for acrylonitrile gives a yearly production rate of about 6000 MM lbs/year of waste. A typical flow rate is about 155 gallons per minute.(8)

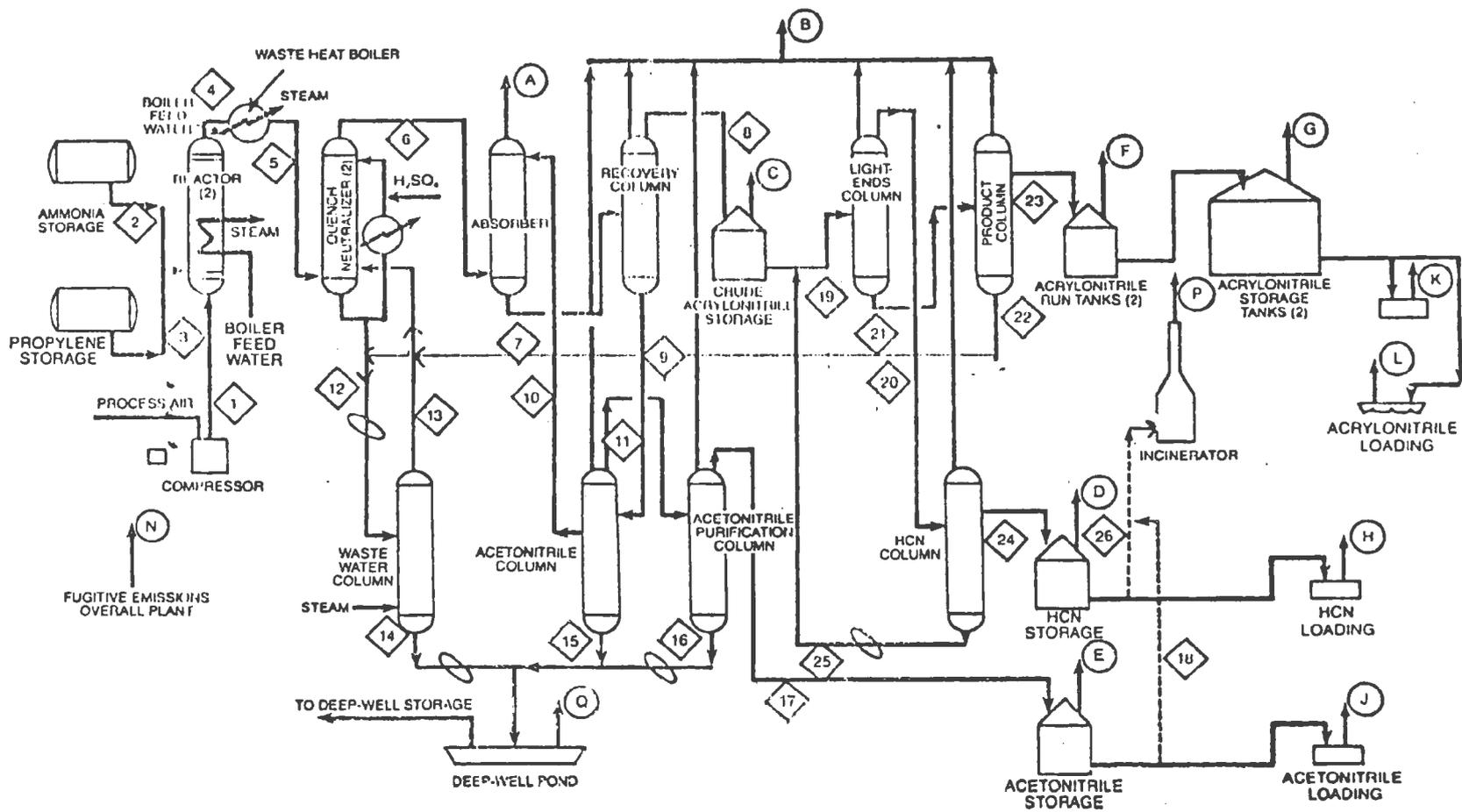


Figure 1. FLOWSHEET FOR ACRYLONITRILE PRODUCTION BY THE SOHIO PROCESSES (6)

Table 2 summarizes the composition of this waste stream. The waste constituents of concern are acrylonitrile, acetonitrile, and hydrocyanic acid.

TABLE 2

Typical Composition of Aqueous Bottom Stream from Wastewater Stripper (8)

	mg/l
Acrylonitrile	500 or less
Acetonitrile	3,000
HCN	7,000
Sulfates	32,000
Ammonia	15,000
Additional non-toxic solids	40,000 approximately

Wastewater stripper column bottoms are sent to a settling pond where they are co-mingled with other process wastes. After the solids settle, the liquid waste is injected into disposal wells.(8) The acrylonitrile facility which deviates from this process is duPont in Memphis. At this facility, the wastes are treated by alkaline hydrolysis. The biodegradable effluent is disposed of in a municipal sewer.(8)

2. Bottom Stream from Acetonitrile Column (Stream 15, Figure 1).

The crude acetonitrile obtained as bottoms from the recovery column goes to the acetonitrile column for separation of water (which is recycled to the absorber). This waste stream is also aqueous.

This stream is typically produced at a rate of 1003 g. per kg. acrylonitrile product.<sup>(6)</sup> Applying this factor to the total nameplate capacity of the acrylonitrile producers who are recovering acetonitrile results in an upper limit estimate of 675 MM lb. of the waste stream produced per year. At the Vistron plant, approximately 180 gallons per minute of column bottoms are produced.<sup>(8)</sup>

A typical composition of this waste stream is shown in Table 3.

TABLE 3

Typical Composition of Bottom Stream from Acetonitrile Column <sup>(8)</sup>  
(waste constituents of concern only)

	mg/l
HCN	225
Acrylonitrile	<10
Acetonitrile	35

This waste stream is combined with other process wastes (streams 14 and 16, Figure 1) and sent to a settling pond, followed by final disposal, as previously described (see page 6).

3. Bottoms from Acetonitrile Purification Column (Stream 16, Fig. 1).

This stream is generated in the purification of crude acetonitrile obtained as bottoms from the recovery column, after water separation in the acetonitrile column. This waste stream is not expected to be present in large quantities, since acetonitrile is a minor by-product of acrylonitrile production.

The waste is expected to contain substantial concentrations of acetonitrile (since purification would probably not be complete), and acrylamide (which as a heavy compound would be found in the purification residue). This waste is generally mixed with aqueous process waste and sent to the settling pond, followed by final disposal (see page 6).

Although waste streams 14, 15, and 16 (the two aqueous bottom wastes, and the acetonitrile purification column bottoms) are reported to be mingled in process and co-disposed, the Agency has determined to list each waste stream separately for purposes of clarity. There may also be situations of which the Agency is unaware when one or another of these waste streams is not co-disposed, in which case the individual listing description prevents a lapse in regulatory coverage.

### III. Discussion of Basis for Listing

#### A. Toxicity Hazard Posed by Wastewater Stripper Stream, Acetonitrile Column Stream, and Acetonitrile Purification Column Bottoms

These three waste streams are commonly co-mingled in a single settling pond, where solids are allowed to settle (see page 6), and therefore are discussed together. The wastes are certainly capable of creating a substantial hazard if improperly ponded.

As described above, these waste streams contain acrylonitrile, a substance identified by the Agency as exhibiting substantial evidence of being carcinogenic; acrylamide, which is regulated by OSHA as a carcinogen; highly toxic hydrocyanic acid; and acetonitrile, which is also toxic (see page 13 below). These waste constituents are deemed to be present in sufficient concentrations to be of regulatory concern. Even in

these highly diluted waste streams\*, acrylonitrile is present in concentrations up to 500 ppm (Table 2, p. 6).\*\* Hydrocyanic acid may be present in concentrations of 7000 ppm. Concentrations of these constituents in pond sediments are likely to be significantly higher, since pond sediments are much more concentrated than aqueous waste streams.

These wastes are also generated in very substantial quantities. Thus, the quantities of hydrocyanic acid, acrylonitrile and acetonitrile discharged to a common holding pond annually, from just one plant, are very substantial.(8)

<u>Compound</u>	<u>Amount/Year</u>
Hydrocyanic Acid	5 million pounds
Acrylonitrile	300,000 pounds
Acetonitrile	2 million pounds

Very large amounts of hazardous waste constituents are thus potentially available for environmental release. If mismanagement occurs, large expanses of groundwater, surface water and soils may be contaminated. Contamination will probably be prolonged, since large amounts of pollutants are available for loading. Site attenuative capacity may be exhausted as well, again increasing the risk of exposure. All of these factors strongly support the listing.

Waste constituents, moreover, have high migratory potential. Acrylonitrile, acrylamide, and acetonitrile are all highly soluble (App. B). (Acetonitrile, in fact, is miscible.(46)) In addition,

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\*Acetonitrile purification column bottoms are not aqueous, but probably are mixed with other aqueous waste streams, and so are included in the discussion in the text.

\*\*The Agency policy is that carcinogens have no safe level of exposure. See 44 FR 15926, 15930 (March 1979). Thus, minute concentrations of carcinogens may well be of regulatory concern. In any case, the Agency regards acrylonitrile concentrations in these wastes to be relatively substantial for purposes of making a hazardousness determination.

acrylamide and acrylonitrile tend to volatilize (46), and so could pose a hazard via an air inhalation pathway. They may be highly mobile as well, particularly in areas with highly permeable soils, or where soils are low in organic content.(46) Acrylamide has in fact been documented to have moved from a sewer grouting operation through the soil to a private water well.(18) These waste constituents also may persist after migrating from the waste site. The major degradation mechanism for acrylamide and acetonitrile is biodegradation(46), which would not affect these constituents in the abiotic conditions of an aquifer. Acetonitrile also degrades (although slowly) to highly toxic cyanide (46), increasing the opportunity for hazard if it is released. The major degradation mechanism for acrylonitrile is photodetoxification(13,14), which again would not affect this compound's persistence in groundwater.

Hydrocyanic acid, the other major waste constituent, is also highly mobile and persistent. Free cyanides, which may migrate from these wastes, have been shown to be extremely mobile in soil; pH appears to influence the mobility with greater mobility at high pH.(11) Also, cyanide has been shown to move through soils into groundwater.(14) In surface waters, cyanide often volatilizes. The hydrogen cyanide vapors pose a hazard to workers or nearby populations because of their extreme toxicity.

An actual damage incident involving wastes containing hydrocyanic acid confirm that cyanide can migrate, persist and contaminate groundwater, public drinking water, and soil. A landfill in Monroe County, Pennsylvania, that accepts plating process wastes such as hydrocyanic acid, has created a groundwater pollution problem in the area.(44)

Thus, these wastes could clearly create a substantial hazard via a groundwater exposure pathway if improperly ponded, or if concentrated liquid from the holding pond is improperly well injected. Improper ponding also could result in a hazard via a surface water pathway. If flooding occurs due to heavy rainfall, these hazardous chemicals could enter surface water unless adequate waste management methods are utilized. As most of the acrylonitrile plants are located in Texas and Louisiana Gulf Coast area where average yearly rainfall is heavy and the groundwater is close to the surface, the likelihood of groundwater contamination is very high.

The Agency therefore regards these three wastes as toxic.

B. Reactivity Hazard Posed by Wastewater Stripper Stream and Acetonitrile Column Stream

Both of these waste streams contain hydrocyanic acid, which is hydrogen cyanide gas in liquid form. If these wastes are exposed to relatively mild acidic conditions, hydrogen cyanide gas will be released. The wastes thus meet the characteristic of reactivity contained in Part 261.23(a)(b) and are listed accordingly.

IV. Health and Ecological Effects

1. Acrylonitrile

Health Effects - Industry-sponsored studies and other studies of data on exposed workers and animal tests strongly indicate that acrylonitrile is carcinogenic in humans.<sup>(20,24)</sup> It has also been identified by the Agency as a compound exhibiting substantial evidence of being a carcinogen. Evidence has also developed from positive laboratory tests in

several organisms that acrylonitrile is a mutagen.(25,27) It has also been reported to be teratogenic and toxic to mothers.(29) Acrylonitrile is an extremely toxic chemical by inhalation, ingestion, or dermal routes following exposure to small quantities (oral rat LD<sub>50</sub>=82mg/kg.); it is rapidly absorbed and distributed widely in the body, and acts by damaging respiratory processes (causing asphyxia) and many tissues in a manner similar to cyanide poisoning.(30,33)

Ecological Effects - The fathead minnow has an observed 96-hour LC-50 of 10-18 mg/l.(34) A bluegill in a 28-day study bioconcentrated acrylonitrile 48-fold(35).

Priority Pollutant - Acrylonitrile is designated as a priority pollutant under Section 307(a) of the CWA.

Regulations - Acrylonitrile is regulated by the Office of Water and Waste Management under the Clean Water Act (304(a) and 311). The Office of Toxic Substances has regulated acrylonitrile under FIFRA and has requested additional testing under Section 4 of the Toxic Substances Control Act. The OSHA TWA is 2 ppm.

Industrial Recognition - Sax, Dangerous Properties of Industrial Materials designates acrylonitrile as highly toxic by oral and dermal routes. The Handbook of Industrial Toxicology designates acrylonitrile as extremely toxic via ingestion, inhalation, and percutaneous routes. Additional information on the adverse effects of acrylonitrile can be found in Appendix A.

2. Acrylamide

Health Effects - Acrylamide is regulated by OSHA as a carcinogen under OSHA Standard 1910.1000(g). Acrylamide is a highly toxic chemical by

inhalation, ingestion or dermal routes (oral rat LD<sub>50</sub>=170 mg/Kg).

Fatal intoxication has been reported following industrial exposure.(37)

The ability of acrylamide to alkylate tissue proteins and nucleic acids would suggest that investigations in these areas are necessary.(36)

Regulations - Acrylamide is regulated by OSHA as a carcinogen under OSHA Standard 1910.1000(g). The Office of Toxic Substances has requested additional information and testing under Section 4(e) of TSCA. The OSHA TWA is 300 micro-g/m<sup>3</sup> (skin).

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, recognizes acrylamide as a highly toxic hazard upon ingestion, inhalation and skin absorption.

3. Hydrocyanic Acid/Hydrogen Cyanide (HCN)

Health Effects - Hydrocyanic acid in acrylonitrile production wastes is extremely toxic to humans and animals via ingestion, causing interference with respiration processes leading to asphyxiation and damage to several organs and systems. Toxic effects have been reported in humans at the very low exposure level of less than 1 mg/kg.(40,41) Human poisonings,

including several involving deaths, have been reported since the 1920's. HCN in gaseous state is extremely toxic ( $LC_{50} = 544$  ppm.) to humans. In addition the U.S. Public Health Service established a drinking water standard of 0.2 mg/l as an acceptable level for cyanide in water supplies.

Priority Pollutant - Cyanide is a priority pollutant under Section 307(a) of the CWA.

Regulations - The OSHA permissible limit for exposure to HCN is 10 ppm (skin) ( $11 \text{ mg/m}^3$ ) as an eight hour time weighted average. DOT requires a label stating that HCN is a poisonous and flammable gas.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials lists HCN as highly toxic through ingestion, inhalation and skin absorption. Additional information on the adverse effects of cyanide can be found in Appendix A.

#### 4. Acetonitrile

Exposure to acetonitrile occurs primarily through vapor inhalation and skin absorption. Exposure may cause liver and kidney damage, disorders of the central nervous system, cardiovascular system and gastrointestinal system. It is the release of the cyanide from acetonitrile that is believed to cause these effects. Acute poisoning and death have occurred in workers inhaling acetonitrile in industry.<sup>(48)</sup> Acetonitrile is a component of cigarette smoke and is absorbed by the oral tissues.<sup>(47,50)</sup> Nitriles and their metabolic products have been detected in the urine, blood, and tissues.<sup>(50)</sup> In a two year study with rats, carcinogenesis was not shown for the chemical.<sup>(49)</sup> Mutagenic

effects have not been demonstrated. Teratogenic effects in rats include fetal abnormalities in pregnant rats<sup>(49)</sup> and skeletal abnormalities.<sup>(53)</sup> From chronic exposure, rat developed liver and kidney lesions, and monkeys showed poor coordination.<sup>(52)</sup> Until recently, acetonitrile has been investigated by toxicologist chiefly because of its relationship to thyroid metabolism.<sup>(51)</sup>

#### IV. References

1. Not used in text.
2. Stanford Research Institute. 1979 Directory of chemical producers. SRI International. Menlo Park, California. 1979.
3. Blackford, Judith L. Chemical conversion factors and yields. Chemical Information Services. Stanford Research Institute. Menlo Park, California. 1977.
4. Lowenheim, F.A. and M.K. Moran. Faith, Keyes & Clark's industrial chemicals. 4th ed. John Wiley and Sons, New York. 1975.
5. Not used in text.
6. Hobbs, F. D. and J. A. Key. Emission control options for the synthetic organic chemicals manufacturing industry. Acrylonitrile Product Report. EPA Contract 68-02-2577. Hydrosience. August, 1978. (Draft)
7. Hughes, T. W., and D. A. Horn. Source assessment: Acrylonitrile manufacture (air emissions). EPA No. 600/2-77-107j. September, 1977.
8. Lowenbach, W., and J. Schlesinger. Acrylonitrile manufacture: Pollutant prediction and abatement. Mitre Technical Report MTR-7752. February, 1978.
9. Not used in text.
10. Not used in text.
11. Alessi, B.A., and W.H. Fuller. The mobility of three cyanide forms in soil. pp. 213-223. In: Residual management by land disposal. W.H. Fuller, ed. Environmental Protection Agency. Cincinnati, OH. NTIS PB No. 256 768. 1976.
12. Not used in text.
13. U.S. EPA. Water-related environmental fate of 129 priority pollutants. EPA No. 440/4-79-029a. 1979.
14. U.S. EPA. The prevalence of subsurface migration of hazardous chemical substances at selected industrial waste land disposal sites. EPA No. 530/SW-634. 1977.
15. Not used in text.
16. Not used in text.

17. Not used in text.
18. Igisu, Hideki, et al. Acrylamide encephaloneuropathy due to well water pollution. J. of Neurology, Neurosurgery and Psychiatry 38:581-584. 1975.
19. Not used in text.
20. O'Berg, M. Epidemiologic studies of workers exposed to acrylonitrile: preliminary results. E.I. duPont de Nemours. 1977.
21. Not used in text.
22. Not used in text.
23. Not used in text.
24. Maltoni et al. Carcinogenicity bioassays on rats of acrylonitrile administered by inhalation and by ingestion. La Medicina del Lavoro 68:401. 1977.
25. Benes and Sram. Mutagenic activity of some pesticides in Drosophila melanogaster. Ind. Med Surg 38:442. 1969.
26. Not used in text.
27. Venitt, et al. Mutagenicity of acrylonitrile (cyanoethylene) in Escherichia coli. Mut. Res. 45:283. 1977.
28. Not used in text.
29. Murray F.J., et al. Teratogenicity of acrylonitrile given to rats by gavage or by inhalation. Ed. Cosmet. Toxicol. 16:547-551. 1978.
30. NIOSH. A recommended standard for occupational exposure to acrylonitrile. NIOSH #78-166. 1978.
31. Not used in text.
32. Not used in text.
33. Sakurai, H., and M. Kusumoto. Epidemiological study of health impairment among acrylonitrile workers. Rod. Kagaku 48:273. 1972.
34. Henderson, et al. The effect of some organic cyanides (nitriles) on fish. Eng. Bull. Ext. Ser. Purdue Univ. No. 106:130. 1961.
35. U.S. EPA. In-depth studies on health and environmental impacts of selected water pollutants. U.S. EPA. Contract 68-01-4646. 1979.

36. Not used in text.
37. U.S. EPA. Investigation of selected environmental contaminants: Acrylamides. NTIS PB No. 257 704. 1976.
38. NIOSH. Registry of toxic effects of chemical substances. DHEW Pub. No. 79-100. p. 51. 1978.
39. Not used in text.
40. NIOSH. Criteria for recommended standard occupational exposure to HCN and cyanide salts. #77-108. 1976.
41. Henderson, et al. The effect of some organic cyanides (nitriles) on fish. Eng. Bull. Ext. Ser. Purdue University. No. 106:130. 1961.
42. Not used in text.
43. Not used in text.
44. U.S. EPA. Open files. Hazardous Site Control Branch, WH-548, U.S. EPA. 401 M St., S.W., Washington, D.C. 20460. Contact Hugh Kauffman. (202) 245-3051.
45. Not used in text.
46. Not used in text.
47. Dalhamn, T., et al. Mouth absorption of various compounds in cigarette smoke. Arch. Environ. Health 16:831. 1968.
48. Dequidt, J., et al. Intoxication with acetonitrile with a report on a fatal case. Eur. J. Toxicol. 7:91. 1974.
49. Not used in text.
50. McKee, H.C., et al. Acetonitrile in body fluids related to smoking. Public Health Rep. 77:553. 1962.
51. Patty, F. A., ed. Industrial hygiene and toxicology. V.II. Interscience Publishers, New York. 1963.
52. Pozzani, V.C., et al. An investigation of the mammalian toxicity of acetonitrile. J. Occup. Med. 1:634. 1959.
53. Schmidt, W., et al. Formation of skeletal abnormalities after treatment with aminoacetonitrile and cyclophosphamide during rat fetogenesis. Verh. Anat. 71:635-638(Ger.) Chem. Abst. 1515w. 1976.

Response to Comments - Bottom Stream from the Wastewater Stripper, Still Bottoms from the Final Purification of Acrylonitrile, Bottom Stream from the Acetronitrile Column and Bottoms from the Acetronitrile Purification Column in the Production of Acrylonitrile

A number of comments were received with respect to wastes K011 to K014 (wastes generated in the production of acrylonitrile).

1. One commenter felt that the Agency has improperly placed the responsibility for determining the degradability of acrylonitrile and acrylamide for these particular wastes in the de-listing process rather than in the listing process (i.e., the commenter believes that acrylonitrile and acrylamide, two of the constituents of concern in these listings are "readily degradable" in the environment). The commenter also disagrees with the Agency that acrylonitrile and acrylamide are toxic to fish. The commenter, therefore recommends that both acrylonitrile and acrylamide be deleted as a basis for listing wastes K011 to K014. Further, the commenter notes that both the Health and Environmental Effects profile for acrylamide and the CAG carcinogen report for acrylonitrile were unavailable for comment.

The Agency disagrees with the commenter's unsubstantiated claims as to degradability. In the listing background document, the Agency has clearly discussed the degradability or non-degradability of these compounds in the environment. In summary, the major degradation mechanisms for acrylonitrile and acrylamide are biodegradation and photodetoxification, respectively, neither of which would be strongly operative in the abiotic conditions of an aquifer.

Acrylamide has in fact been documented to contaminate groundwater (a private water well). If these wastes were improperly managed, they could clearly create a substantial hazard via a groundwater exposure pathway. This point is especially true for these wastes since most of the acrylonitrile plants are located on the Texas and Louisiana Gulf Coast area where the average yearly rainfall is heavy and the groundwater is close to the surface. Therefore, the probability that these toxic constituents will migrate and reach an abiotic environment and not degrade is high.

With respect to the aquatic toxicity of the two constituents, the Agency agrees with the commenter that both acrylonitrile and acrylamide are not toxic to fish. In the Registry of Toxic Effects (1975 Edition), a widely used reference book which is published by the National Institute for Occupational Safety and Health (NIOSH), a rating of the aquatic toxicity or non-toxicity of chemical substances is provided. In this rating, substances with an LC<sub>50</sub> of between 10,000 ug/l to 100,000 ug/l are considered slightly toxic [acrylonitrile (96-hr LC<sub>50</sub> 10-18 mg/l) and acrylamide (89-100 mg/l)]. Therefore, the Agency will modify the listing background and delete all reference to both acrylonitrile and acrylamide as being toxic to fish. However, both these compounds are recognized as carcinogens: acrylamide is regulated by OSHA as carcinogenic while acrylonitrile has been recognized by the Cancer Assessment Group to be carcinogenic. Consequently, the Agency believes that both of these compounds are sufficiently toxic to present potential harm to human health and the environment, and will continue to

include both acrylonitrile and acrylamide as constituents of concern in these particular listings.

Finally, the Agency admits that the Health and Environmental Effects profile for acrylamide and the CAG carcinogen report for acrylonitrile were unavailable for comment when the regulations were promulgated. However, the Agency strongly believes that sufficient information on the toxicity/carcinogenicity of these two compounds were presented in the listing background document for acrylonitrile production and the Health and Environmental Effects profile on acrylonitrile to support the inclusion of these toxic constituents. It should be noted that the CAG carcinogen report for acrylonitrile has been available for review since June, 1980.

2. One commenter requested that the Agency reassess the listing of "Still bottoms from the final purification of acrylonitrile in the production of acrylonitrile" (K102) as hazardous in Section 261.32. The commenter pointed out that this particular stream is an integral part of the acrylonitrile manufacturing process and does not meet the "sometimes discarded" provision of Section 261.2(b)(3); therefore, they argued that waste K012 should be removed from the list of hazardous wastes.

In re-assessing the ultimate disposition of this particular waste, the Agency agrees with the commenter and, therefore, has removed waste K012 from the hazardous waste list. In contacting all the producers of acrylonitrile, the Agency has learned that this stream meets the provision in Section 261.2(c)(3), "an inter-

mediate manufacturing or mining product which results from one of the steps in a manufacturing or mining process and is typically processed through the next step of the process within a short time." More specifically:

American Cyanamid Co. (New Orleans, La.) - still bottoms from the final purification of acrylonitrile are recycled back into the quench neutralizer which then flows into the wastewater column.

E.I. DuPont de Nemours and Co., Inc. (Memphis, Tenn. and Beaumont, TX.)- still bottoms from the final purification of acrylonitrile are routed directly to the wastewater column.

Monsanto Co. (Cholocate Bayou and Texas City; TX) - still bottoms from the final purification of acrylonitrile are routed directly to the wastewater column.

Vitron Corp. (Lima, Ohio) - still bottoms from the final purification of acrylonitrile are routed directly to the wastewater column.

## LISTING BACKGROUND DOCUMENT

### BENZYL CHLORIDE

#### Still Bottoms from the Distillation of Benzyl Chloride (T)

##### I. Summary of Basis for Listing

Production of benzyl chloride results in the generation of still bottoms which contain hazardous aromatic compounds that include toxic organic substances, carcinogens and suspected carcinogens. The waste constituents of concern are benzyl chloride, toluene, chlorobenzene, and benzotrichloride.

The Administrator has determined that the still bottoms from benzyl chloride production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. Still bottoms from the distillation of benzyl chloride contain benzyl chloride, benzotrichloride (when the dark chlorination, (i.e., catalytic light process is used), toluene, and chlorobenzene isomers. Benzyl chloride has been identified as a carcinogen and a mutagen; the other compounds are toxic.
2. Total quantities of benzyl chloride and benzotrichloride generated per year in this waste equal approximately 90,000 pounds.
3. Disposal of waste in improperly designed or operated landfills could result in substantial hazard via groundwater or surface water exposure pathways. Disposal by incineration, if mismanaged, can also result in serious air pollution through release of hazardous vapors, due to incomplete combustion. Storage of the wastes before incineration presents a potential for contamination of surface or groundwater.
4. The hazardous waste constituents such as chlorobenzene are likely to persist in the environment and to bioaccumulate in environmental receptors.

## II. Sources of the Waste and Typical Disposal Practices

### A. Profile of the Industry

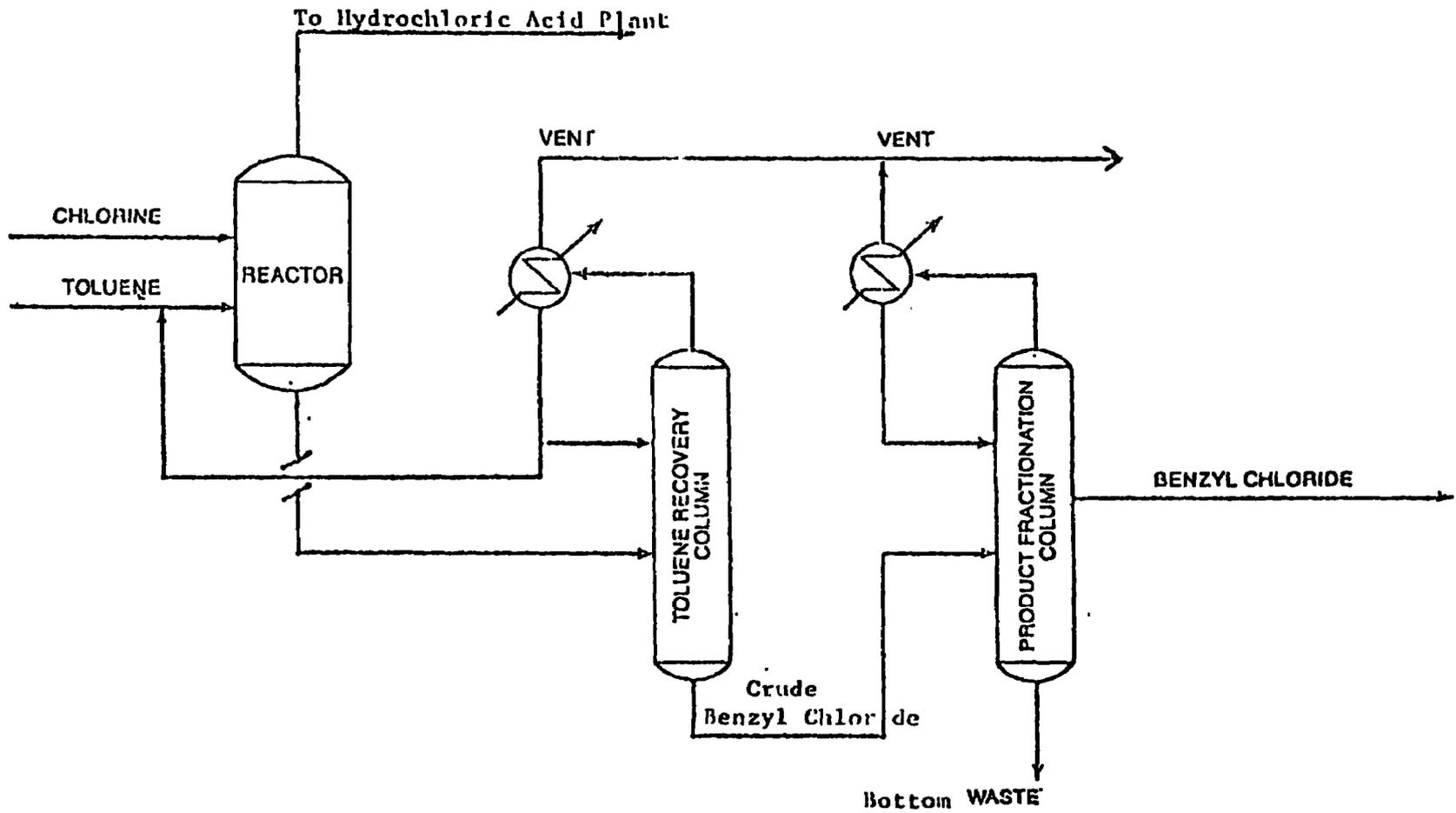
Benzyl chloride ( $C_6H_5CH_2Cl$ ) is used as a raw material for pharmaceuticals and as an intermediate in the preparation of p-benzylphenol and benzyl alcohol.<sup>(1)</sup> The major use for the chemical, however, is in the production of butyl benzyl phthalate, which is a plasticizer used in the manufacture of vinyl products.<sup>(2)</sup>

Significant production of benzyl chloride is reported by two plants responding to the Clean Water Act Section 308 BAT questionnaire of 1979. These plants reported only one process route: toluene chlorination. Total reported production was 223,000 lb/day (100,000 kg/day), which is equivalent to 73.6 million lb/yr (33.4 million kg/yr).<sup>(5)</sup> Both plants that reported production of benzyl chloride also provided data on average production per day. Individual plant production ranges from 25,000 to 198,000 lb/day (11,400 to 89,900 kg/day), and averages 112,000 lb/day (50,600 kg/day).<sup>(5)</sup>

### B. Manufacturing Process (1,2)

Benzyl chloride is produced from the chlorination of toluene. Chlorination may either be by UV light (photochlorination) or by the catalytic process. Catalytic chlorination requires more severe reaction conditions. There are certain differences in waste composition depending on which type of chlorination is used. These differences are described more fully below. The overall process, however, may be generally described.

Chlorine is fed to a heated reactor containing boiling toluene (see Figure 1). For production of benzyl chloride, the reaction is allowed to continue until there is a 37.5% increase in weight; at this point, a mild alkali is added to neutralize the acid formed. The by-product hydrogen chloride vapors



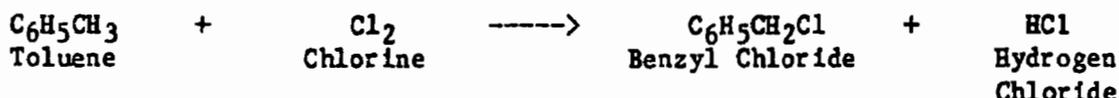
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Figure 1. BENZYL CHLORIDE BY THE CHLORINATION OF TOLUENE

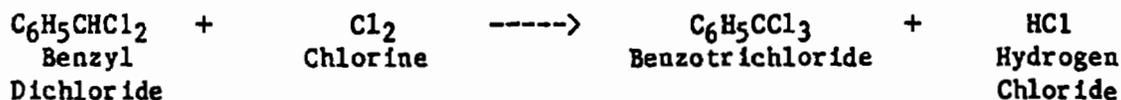
Modified from (1,2)

from the reactor may be passed to a hydrochloric acid plant or recovered as compressed gas.

The following equation shows the main reactions:



One side reaction is as follows:



Reactor products are passed to a toluene-removal vacuum distillation column, where unreacted toluene is removed overhead and recycled to the reactor. Crude benzyl chloride from the bottom of the toluene column is then purified under vacuum in the product-fractionation column. Here, benzyl chloride product is drawn off as a sidestream and the listed waste stream, the still bottom stream, is generated.

### C. Waste Composition, Generation and Management

#### 1. Waste Composition and Generation

The still bottoms waste consists predominantly of chlorinated benzene molecules. If the photochlorination process is used, waste constituents will be benzal chloride (not a waste constituent of concern), and smaller concentrations of benzyl chloride (the product), a range of chlorinated benzenes (from toluene feed stock impurities), and some residual feedstock toluene.<sup>(2)</sup> The chlorinated benzenes in the still bottoms will probably be chiefly the heavier chlorinated benzenes (tri, tetra, penta, and hexa) since lighter chlorobenzenes will go overhead with the product.

It is estimated that benzal chloride will be present in concentrations of .02 kg/kg product, and additional constituents will be present in concentrations of .005 kg/kg product. (Modified from 2, 23)

If the liquid phase catalytic chlorination process is used, these same waste constituents will be present.<sup>(2)</sup> In addition, benzotrichloride will be formed due to the severer reaction conditions.<sup>(2)</sup> (The reaction pathway for benzotrichloride is indicated on p. 3 above.) Benzotrichloride and benzal chloride are expected to be present in the still bottoms in the amount of 0.01 kg/kg and 0.1 kg/kg respectively. (Modified from 2, 23)

Waste quantities are expected to be significant. To gain a rough idea of waste loading, one can assume that half the industry uses the photochlorination process while the other half uses the catalytic process. Therefore, based on total industry annual production of 33.4 million kg (p.2), waste loads from the catalytic process will be over 2 million kg annually (assuming benzal chloride is not recovered) with hazardous waste constituent loading exceeding 200,000 kg a year. Wastes from the photochlorination process would be generated in quantities of approximately 3.3 million kg annually (assuming benzal chloride is not recovered), with hazardous waste loadings of approximately 80,000 kg annually.

## 2. Waste Management

Two operating benzyl chloride plants reported that incineration of the waste was their usual practice.<sup>(24)</sup> A third company is temporarily using landfills until incineration equipment can be obtained.<sup>(24)</sup> Because of the high chlorine content of the waste, an incinerator with alkali scrubbing of off-gases is necessary for proper environmental control.

During incineration, supplemental fuel is usually necessary because of the small heat content of the waste. Flame-out and consequent release of unburned toxic chlorinated hydrocarbons is not uncommon in such situations.

### III. Discussion of Basis for Listing

#### A. Hazards Posed by the Waste

As noted above, the principal waste components are benzyl chloride and benzotrichloride. Toluene and chlorobenzene are also reported to be present, since they are present as feedstock materials. Benzyl chloride has been identified as a carcinogen and benzotrichloride is structurally similar to other demonstrated carcinogens. (See pp. 9-11 following.) Chlorobenzene and toluene are toxic chemicals.

##### 1. Exposure Pathways

As noted, the typical disposal method for these wastes is discharge to a holding pond or other temporary storage area prior to incineration. One company currently landfills these toxic wastes.

The waste constituents of concern may migrate from improperly designed or managed holding ponds or landfills and contaminate ground and surface waters. First of all, the waste constituents are soluble in significant concentrations. Benzyl chloride is extremely soluble in water (solubility 330,000 mg/l), while toluene and chlorobenzene are also very soluble (470 mg/l and 488 mg/l respectively). (Appendix B.) Toluene would also tend to promote solubilizing of other waste constituents, since it is a widely-used commercial solvent. Thus, these waste constituents could leach into groundwater if holding ponds or landfills are inadequately designed and constructed, or lack adequate leachate collection systems.\* Siting of waste management facilities in areas with highly permeable soils could likewise facilitate leachate migration. Disposal or storage in improperly designed or managed ponds

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\*Some of these waste constituents' mobility are effected by certain soil attenuation mechanisms. (App. B) Pollutant mobility could be high, however, where soil attenuation would be slight; for example, where soil is low in organic content, highly permeable, or where attenuative capacity is exhausted.

could similarly promote leachate formation and migration (indeed, the large quantity of percolating liquid available could facilitate environmental release by acting as a hydraulic head).

There is also a danger of migration into and contamination of surface water if holding ponds are improperly designed or managed. Inadequate flood control measures could result in washout or overflow of ponded wastes.

The migratory potential of chlorobenzenes and toluene is confirmed by the fact that chlorobenzenes (mono, di, tri, tetra, and penta) and toluene have all been detected migrating from the Love Canal site into surrounding residential basements and solid surfaces, demonstrating ability to migrate through and persist in soils. ("Love Canal Public Health Bomb", A Special Report to the Governor and Legislature, New York State Department of Health (1978)). Benzyl chloride, although subject to hydrolyzation (App. B), has also been identified as leaching from the Hyde Park Site. (OSW Hazardous Waste Division, Hazardous Waste Incidents, Open File, 1978.)

Once these three contaminants migrate from the matrix of the waste, they are likely to persist in groundwater (see App. B). Chlorobenzene, toluene, and benzyl chloride have in fact been shown to persist in soil and groundwater, as demonstrated by the above-described damage incidents.\*

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\*The above discussion does not consider benzotrighloride, another waste constituent of concern. This waste constituent is relatively insoluble, not very volatile, and tends to degrade in water. It is, however, relatively bioaccumulative (App. B). Thus, this waste constituent shows a lesser propensity to migrate and reach environmental receptors, but could accumulate in harmful concentrations if it reached a receptor. Furthermore, benzotrighloride has been identified as migrating from the Love Canal site (OSW Hazardous Waste Division, Hazardous Waste Incidents, *supra*), demonstrating some ability to migrate and persist if improperly managed.

There also may be a danger of migration and exposure via an air inhalation pathway if disposal sites lack adequate cover. Toluene is relatively volatile (App. B), and is mobile and persistent in air, having been found in school and basement air at Love Canal ("Love Canal Public Health Bomb", supra). Chlorobenzenes and benzyl chloride, while less volatile (App. B), are also mobile and persistent in air. Chlorobenzene (mono through penta) have been identified in school and basement air at Love Canal ("Love Canal Public Health Bomb," supra), while benzyl chloride has been shown to persist in the atmosphere in the New Jersey area for considerable periods of time.<sup>(6)</sup> Thus, these hazardous constituents could migrate from uncovered landfills or holding ponds and persist for long periods in the environment.

Disposal by incineration, if mismanaged, also can result in serious air pollution through the release of toxic fumes. This may occur when incineration facilities are operated in such a way that combustion is incomplete (i.e., inadequate conditions of temperature, mixing, and residence time) resulting in airborne dispersion of hazardous vapors containing undestroyed waste constituents. This could present a significant opportunity for exposure of humans, wildlife and vegetation in the vicinity of these operations to hazardous constituents through direct contact and also through pollution of surface waters.

The waste constituents in the still bottoms from benzyl chloride production are of the highest regulatory concern. For example, there is no known safe level of exposure for carcinogens (see 44 Fed. Reg. 15926, 15940, (March 15, 1979)). The Administrator would require assurance that these waste constituents could not migrate and persist to justify a determination not to list this waste stream. These waste constituents, to the contrary,

have migrated and persisted to cause substantial hazard in actual instances. The waste is therefore deemed hazardous.\*

B. Health and Ecological Effects

1. Benzyl Chloride

Health Effects - Benzyl chloride has been identified as a carcinogen<sup>(8)</sup>, and is also mutagenic<sup>(9)</sup>. Additional information and specific references on the adverse effects of benzyl chloride can be found in Appendix A.

Regulatory Recognition of Hazard - The OSHA TWA for benzyl chloride is 1 ppm. DOT requires labeling as a corrosive. The Office of Water and Waste Management, EPA, has regulated benzyl chloride under Section 311 of the Clean Water Act. Preregulatory assessment has been completed by the Office of Air, Radiation and Noise under the Clean Air Act. The Office of Toxic Substances has requested additional testing under Section 4 of the Toxic Substances Control Act.

Industrial Recognition of Hazard - Benzyl chloride is listed in Sax's Dangerous Properties of Industrial Materials as highly toxic via inhalation and moderately toxic via the oral route.

2. Chlorobenzene

Health Effects - Chlorobenzene is a toxic chemical absorbed into the body by inhalation, ingestion, and through the skin. Doses of chlorobenzene have been reported to cause liver damage in animals, abnormal dumping of porphyrin pigments from the liver, weakness and stupor. Additional information

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\*Furthermore, the waste constituents are generated in large annual quantities, thus increasing the possibility of exposure if the wastes are managed improperly. These large quantities of hazardous constituents potentially available for release further justify a hazardous listing.

and specific references on the adverse effects of chlorobenzene can be found in Appendix A.

Environmental Effects - Chlorobenzenes are toxic to lower order organisms and aquatic toxicity of chlorobenzene is indicated from studies with saltwater shrimp species. Chlorobenzene has been shown to bioaccumulate in fish(15).

Regulations - The OSHA TWA in air is 75 ppm. Chlorobenzene is designated as a priority pollutant under Section 307(a) of the CWA. (10, 11, 12, 13, 14)

Industrial Recognition of Hazard - Chlorobenzene is listed in Sax's Dangerous Properties of Industrial Materials as a dangerous chlorine compound.

### 3. Toluene

Health Effects - Toluene is a toxic chemical absorbed into the body by inhalation, ingestion, and through the skin. The acute toxic effect of toluene in humans is primarily depression of the central nervous system(16). Chronic occupational exposure in shoe workers was reported to lead to the development of neuro-muscular disorders, such as abnormal tendon reflexes and decreased grasping strength(17). In animal studies, preliminary evidence of bone marrow chromosomal abnormalities was reported(18, 19).

Since toluene is metabolized in the body by a protective enzyme system which is also involved in the elimination of other toxins, it appears that overloading the metabolic pathways with toluene will greatly reduce the clearance of other, more toxic chemicals. Additionally, the high affinity of toluene for fatty tissue can assist in the absorption of other toxic chemi-

cals into the body. Thus, synergistic effects of toluene on the toxicities of other contaminants may render the waste stream more hazardous. Beyond these considerations, toluene, by virtue of its solvent properties, can facilitate mobility and dispersion of other toxic substances, assisting their movement toward ground or surface waters. Toluene is designated as a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of toluene can be found in Appendix A.

Ecological Effects - Toluene has been shown to be acutely toxic to freshwater fish and to marine fish. Chronic toxicity is also reported for marine fish<sup>(20)</sup>. The USEPA recommended criterion levels to protect aquatic life are: freshwater, 2.3 mg/l, and marine, 100 mg/l<sup>(20)</sup>.

Regulations - Toluene has an OSHA standard for air (TWA) of 200 ppm. The Department of Transportation requires a "flammable liquid" label.

Industrial Recognition of Hazard - Toluene is listed as having a moderate toxic hazard rating via oral and inhalation routes (Sax, Dangerous Properties of Industrial Materials).

#### 4. Benzotrachloride

Health Effects - Benzotrachloride is toxic with vapors that are highly irritating to the skin and mucous membranes. In addition, large doses have caused central nervous system depression in experimental animals<sup>(21)</sup>. Inhalation of 125 ppm for 4 hours was lethal to rats<sup>(22)</sup>. Benzotrachloride has been designated as a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of benzotrachloride can be found in Appendix A.

Industrial Recognition of Hazard - Benzotrachloride has a high toxicity rating via inhalation (Sax, Dangerous Properties of Industrial Materials).

#### IV. References

1. Kirk-Othmer. Encyclopedia of chemical technology. 5. John Wiley and Sons, Inc., New York. 1964.
2. Lowenheim, F. A. and M. K. Moran. Faith, Keyes and Clark's industrial chemistry. 4th ed. John Wiley and Sons, Inc., New York. 1975.
3. Not used in text.
4. Not used in text.
5. Individual Plants' Responses to EPA's 308 questionnaire.
6. Altshuller, A. P. Lifetimes of organic molecules in the troposphere and lower stratosphere. Environmental Science and Technology. 1980. In press.
7. Not used in text.
8. Druckrey, H., H. Druse, R. Pruessmann, S. Ivankovic, C. Landschutz. Carcinogenic alkylating substances --- III. Alkyl-halogenides, -sulfates, -sulfonates and strained heterocyclic compounds. Z. Krebsforsch 74:241-70. 1970. (Ger).
9. McCann, J., E. Choi, E. Yamasaki, B. N. Ames. Detection of carcinogens as mutagens in the Salmonella/microsome test - Assay of 300 chemicals. Proc. National Academy of Sciences USA 72:5135-39. 1975.
10. U.S. EPA. Investigation of selected potential environmental contaminants: Halogenated benzenes. EPA No. 560/1-77-004. 1977.
11. Lu, A.Y.H., et al. Liver microsomal electron transport systems. III. Involvement of cytochrome B<sub>5</sub> in the NADH-supported cytochrome p<sup>5</sup>-450 dependent hydroxylation of chlorobenzene. Biochem. Biophys. Res. Comm. 61:1348. 1974.
12. Brodie, B. B., et al. Possible mechanism of liver necrosis caused by aromatic organic compounds. Proc. Natl. Acad. Sci. 68:160. 1971.
13. Knapp, W. R., Jr., et al. Subacute oral toxicity of monochlorobenzene in dogs and rats. Toxicol. Appl. Pharmacol. 19:393. 1971.
14. Irish, D. D. Halogenated hydrocarbons: II. Cyclic. In Industrial hygiene and toxicology. V.II, 2nd ed. F. A. Patty, ed. Interscience. New York. p. 1333. 1963.
15. Lu, P., and Metcalf. Environmental fate and biodegradability of benzene derivatives as studied in a model aquatic ecosystem. Environ. Health Perspect. 10:269-285. 1975.
16. U.S. EPA. Toluene: Ambient water quality criteria. NTIS PB No. 296 805/5BE. 1979.

17. Matsushita, T., et al. Hematological and neuro-muscular response of workers exposed to low concentration of toluene vapor. Ind. Health. 13:115. 1975.
18. Dobrokhotoy, V. B., and M. I. Enikeev. Mutagenic effect of benzene, toluene, and a mixture of these hydrocarbons in a chronic experiment. Gig. Sanit. 1:32. 1977.
19. Lyapkalo, A. A. Genetic activity of benzene and toluene. Gig. Tr. Prof. Zabol. 17:24. 1973.
20. U.S. EPA. Toluene: Hazard profile. Environmental Criteria and Assessment Office, U.S. EPA. Cincinnati, Ohio. 1979.
21. Windholz, M., ed. 1976 Merck Index, 9th ed. Merck and Co., Inc., Rahway, NJ. 1976.
22. Sax, N. I. Dangerous properties of industrial materials, 5th ed. Van Nostrand Reinhold Co., New York. 1979.
23. Groggins. Unit processes on organic synthesis, 2nd ed. 1938.
24. U.S. Department of Health, Education, and Welfare. Criteria for a recommended standard - Occupational exposure to benzyl chloride. Washington, D.C. 1978.

LISTING BACKGROUND DOCUMENT  
CARBON TETRACHLORIDE PRODUCTION

Heavy ends or distillation residues from the production of carbon tetrachloride (T)

I. Summary of Basis for Listing

Heavy ends or distillation residues from carbon tetrachloride production contain carcinogenic and toxic organic substances. These include carbon tetrachloride, hexachlorobutadiene, hexachlorobenzene, perchloroethylene and hexachloroethane.

The Administrator has determined that the solid waste from carbon tetrachloride production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. The heavy ends or distillation residues from the various carbon tetrachloride production processes contain some or all of the following constituents: perchloroethylene, carbon tetrachloride, hexachlorobutadiene, hexachlorobenzene, and hexachloroethane. All of these substances except hexachloroethane have been identified by the Agency as compounds which have exhibited substantial evidence of being carcinogenic; hexachloroethane is a suspect carcinogen. Hexachlorobenzene is also a teratogen. All of these compounds are very toxic as well.
2. Approximately 8.6 million pounds/year of waste containing these hazardous compounds are generated in the United States by six manufacturers at 10 plants.
3. Disposal of these wastes in drums in improperly designed or operated landfills represents a potential hazard due to the probable corrosion of drums and the resulting leaching into groundwater of these hazardous compounds.

4. Mismanagement of incineration operations and volatilization from landfills could result in the release of hazardous vapors to the atmosphere, and present a significant opportunity for exposure of humans, wildlife and vegetation in the vicinity of these operations to potentially harmful substances.
5. The components of concern are persistent in the environment, thus increasing the chance for exposure.
6. The components of concern have been implicated in actual damage incidents.

## II. Sources of the Waste and Typical Disposal Practices

### A. Profile of the Industry

There are six major corporations involved in the production of carbon tetrachloride. The locations and annual capacity for each plant are listed in Table 1.

The current principle use of carbon tetrachloride is in the manufacture of chlorofluoromethanes used in refrigeration and aerosols. Other uses include grain fumigation and a variety of solvent and chemical-manufacturing applications.(2)

### B. Manufacturing Process

Carbon tetrachloride is produced principally via four processes: direct chlorination of methane, pyrolysis or chlorinolysis of hexachloroethane with simultaneous chlorination of perchloroethylene, direct chlorination of propane (in which perchloroethylene is produced as a co-product), and direct chlorination of carbon disulfide. These processes, and the listed waste streams generated thereby, are discussed below.\*(4,2,31)

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\* These processes generally involve production of a range of chlorinated organic products as well as carbon tetrachloride

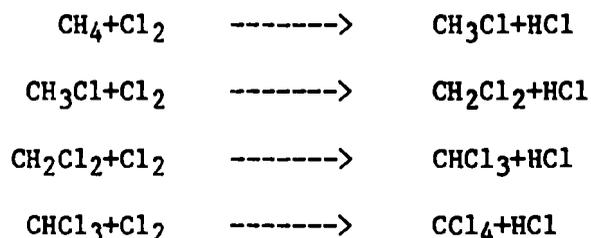
TABLE 1

Plant Sites for Carbon Tetrachloride Production<sup>(3)</sup>

Company	Location	Annual Capacity (Millions of Pounds)
Allied Chemical Corp. Specialty Chemicals Division	Moundsville, WV	8
Dow Chemical, U.S.A.	Freeport, TX Pittsburg, CA Plaquemine, LA	135 80 125
E.I. duPont de Nemours & Co., Inc. Petrochems Dept. Freon® Prod. Div.	Corpus Christi, TX	500
Stauffer Chemical Co. Ind. Chems. Div.	Le Mogue, AL Louisville, KY	200 70
Vulcan Material Co. Chemical Div.	Geismar, LA Wichita, KA	90 60
FMC Corporation	S. Charleston, WV	300
	Total	1,568

1. Direct Chlorination of Methane (31)

The sequence of reactions for production of carbon tetrachloride from the direct chlorination of methane is:



The reaction is conducted adiabatically at temperatures ranging from 350° - 370°C and at approximately atmospheric pressure. In this process, methyl chloride, methylene chloride and chloroform are usually co-produced with carbon tetrachloride. The ratio of formation of these reaction products may be controlled to favor production of higher chlorinated products (e.g., carbon tetrachloride) by recycle of less chlorinated products (e.g., methyl chloride). Typical yields range from 85% to 95% based on methane.

Figure 1 represents a simplified process for production of carbon tetrachloride via direct chlorination of methane. Methane is mixed with chlorine, preheated and fed to a reactor fitted with mercury arc lamps to enhance disassociation of chlorine. Chlorine is the limiting reactant and about 65% of the methane reacts. A typical range of products leaving the reactor is: methyl chloride - 58.5%; methylene chloride - 29.3%; chloroform - 9.7%; and carbon tetrachloride - 2.3%. The effluent gases from the reactor also contain unreacted methane and hydrogen chloride which are separated by scrubbing the reacted gases with a mixture of liquid chloromethanes, usually a refrigerated

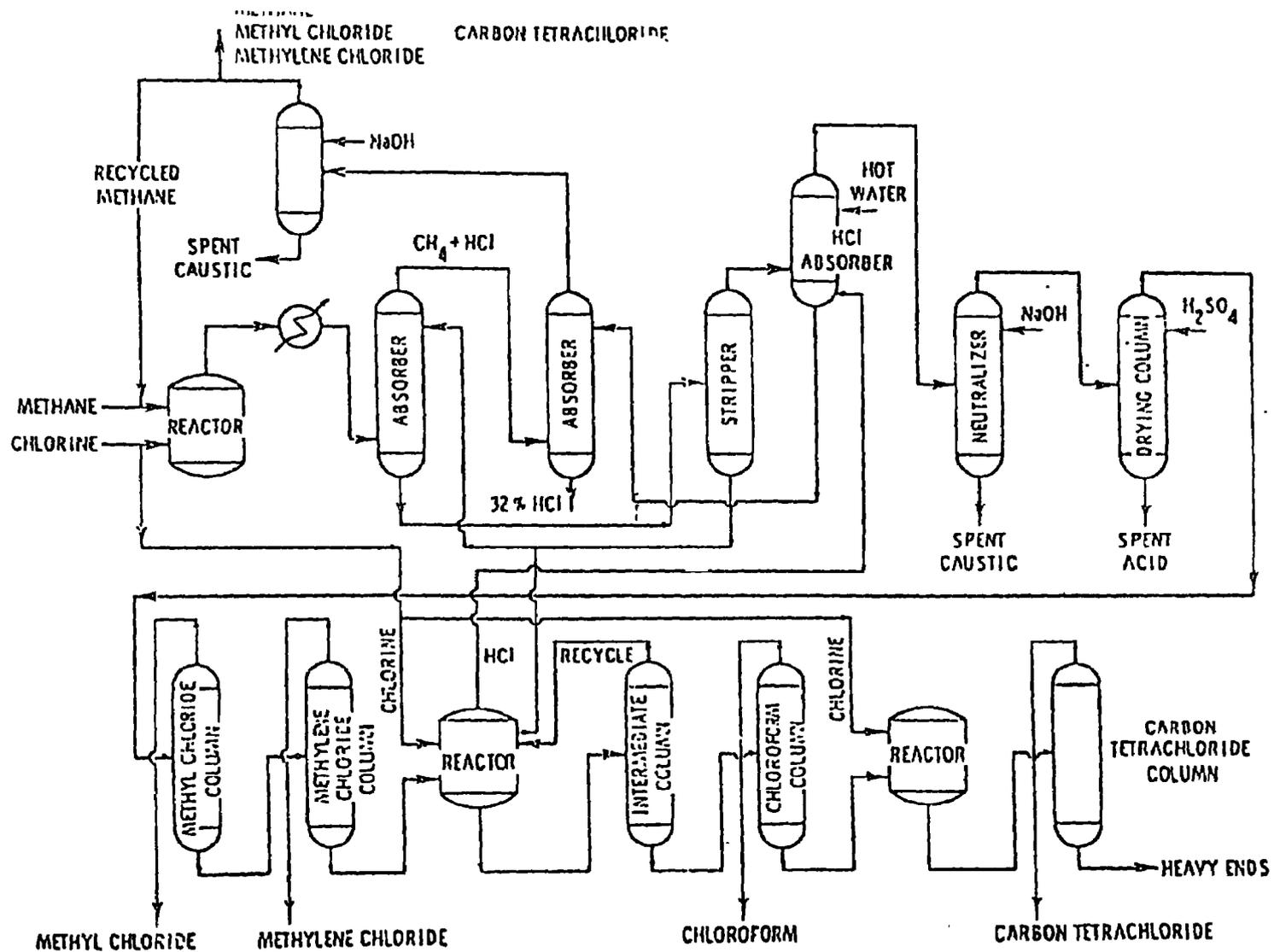


Figure 1. Methyl chloride, methylene chloride, chloroform and carbon tetrachloride by the direct chlorination of methane.

(Modified from 31)

mixture of chloroform and carbon tetrachloride. Methane and hydrogen chloride are not absorbed and go overhead. Hydrogen chloride is removed by scrubbing with water and methane is recycled. The enriched chloromethane solvent absorber effluent is stripped of methyl chloride and some methylene dichloride. The stripped solvent bottoms are recycled to the absorber. The overhead product is condensed and purified successively by a hot water wash (to remove residual hydrogen chloride), an alkali wash, and a strong sulfuric acid wash (to dry the chlorinated organic stream). The stripped methyl chloride, methylene chloride and any heavy ends are separated by fractional distillation.

A portion of the bottoms from the stripping column together with some or all of the recovered methyl chloride and methylene chloride is then fed to a secondary reactor where chlorination is again carried out photochemically, but this time in the liquid phase. Hydrogen chloride is vented from the reactor. The reaction products are purified and separated by a sequence similar to that used for methyl chloride and methylene chloride, except that any product less chlorinated than chloroform may be recycled. Desired quantities of chloroform are removed by distillation, and the remaining material is chlorinated in a third reactor to produce carbon tetrachloride. The effluent from the third reactor is distilled to recover carbon tetrachloride. The heavy bottoms from this tower is the process waste.

Waste constituents predicted to be present in heavy ends from this process in substantial concentrations are hexachloroethane, hexachlorobutadiene, perchloroethylene (tetrachloroethylene), and carbon tetrachloride.\*

\*As presented in Table 2, little or no carbon tetrachloride was recorded found in the air, aqueous and solid emissions. However, based on industry process, this constituent is predicted to be present in the waste. Further, the presence of even very small concentrations of this very potent carcinogen are of concern to the Agency.

Hexachloroethane would result from chlorination of C<sub>2</sub> molecules, which could be formed from methyl radicals. The same general type of reaction would also result in formation of hexachlorobutadienes, except that C<sub>4</sub> molecules (rather than C<sub>2</sub> molecules) would be chlorinated. Perchloroethylene is expected to result from the dechlorination of hexachloroethane.

A literature source estimating emissions from direct chlorination of methane is set forth in Table 2.

## 2. Chlorinolysis of Hydrocarbon Feedstocks

Chlorinolysis\* processes, in fact, make up the bulk of carbon tetrachloride (perchloroethylene is a co-product) capacity in the United States. Feedstocks for this process include aliphatic hydrocarbons (e.g., propane), chlorinated aliphatic hydrocarbons, and chlorinated aromatic hydrocarbons. Use of chlorinated feedstocks is particularly valuable for control of residues from other chlorination processes, which otherwise would pose a difficult disposal problem.

The conditions necessary for chlorinolysis of hydrocarbon feedstocks are somewhat more severe than those of direct chlorination of methane; both higher temperatures and higher molar ratios of chlorine to hydrocarbon are used. The product distribution is quite dependent on the feedstock used and varies from over 90% carbon tetrachloride (propane) to over 90% perchloroethylene (propene).

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\*Chlorinolysis reactions refer to those chlorination reactions which result in extensive rupture of carbon-carbon bonds.

TABLE 2 ESTIMATED EMISSIONS FROM THERMAL CHLORINATION OF METHANE .

Species	EMISSIONS kg/Mg of product <sup>1</sup>		
	<u>Air</u>	<u>Aqueous</u>	<u>Solid</u>
Methane	28	39	
Methyl chloride	trace		
Carbon tetrachloride	0.3		
Perchloroethylene			17
Hexachloroethane			16
Sodium chloride		16	
Sodium hydroxide		0.6	
			33

Source: Wasselle, "Chlorinated Hydrocarbons", Process Economics Program Report No. 126, Stanford Research Institute, Menlo Park, CA, August, 1978.

Based on hydrogen chloride product. To convert from hydrogen chloride product to a specific chlorinated hydrocarbon product, the following factors are used:

- 0.72 lbs HCl/lb CH<sub>3</sub>Cl
- 0.86 lbs HCl/lb CH<sup>3</sup>Cl<sub>2</sub>
- 0.92 lbs HCl/lb CH<sup>2</sup>Cl<sub>3</sub>
- 0.95 lbs HCl/lb CCl<sub>4</sub>

In basic terms, the chlorinolysis involves the fracturing of carbon bonds (at severe reaction conditions), followed by rechlorination of the fractured portions. Waste residues result from incomplete chlorination of the cracked hydrocarbons. Hydrocarbon chlorinolysis reactions thus tend to produce similarly-composed residual wastes. Waste constituents predicted to be generally present are hexachlorobenzene, hexachloroethane, perchloroethylene, hexachlorobutadiene, and carbon tetrachloride. Two principal chlorinolysis processes for the production of carbon tetrachloride are described more fully below.

a. Chlorinolysis of Propane (31)

The basic chemical equation representing the direct chlorination of propane to produce carbon tetrachloride and perchloroethylene is:

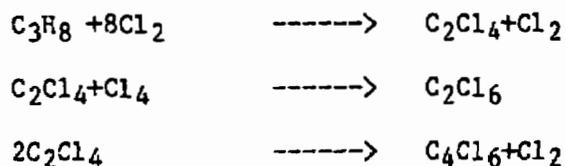


Figure 2 is a simple block flow diagram for the production of carbon tetrachloride and perchloroethylene by the direct chlorination of propane.

Feedstock chlorine, together with recycled chlorine, and propane are introduced into a vaporizer where they are mixed with recycled chlorocarbons. Chlorine is used in approximately 10% to 25% excess. The mixed gases react adiabatically at atmospheric pressure in a refractory-lined reactor at temperatures ranging from 550°C and 700°C (controlled by the diluent action of recycled streams). The recycle ratio also affects the product distribution. Effluent from the reactor (mainly carbon tetrachloride, perchlorethylene, hydrogen chloride, chlorine, and unreacted hydrocarbon) is quenched with perchloroethylene to minimize formation of by-products.

Carbon tetrachloride, separated by fractionation, is condensed and

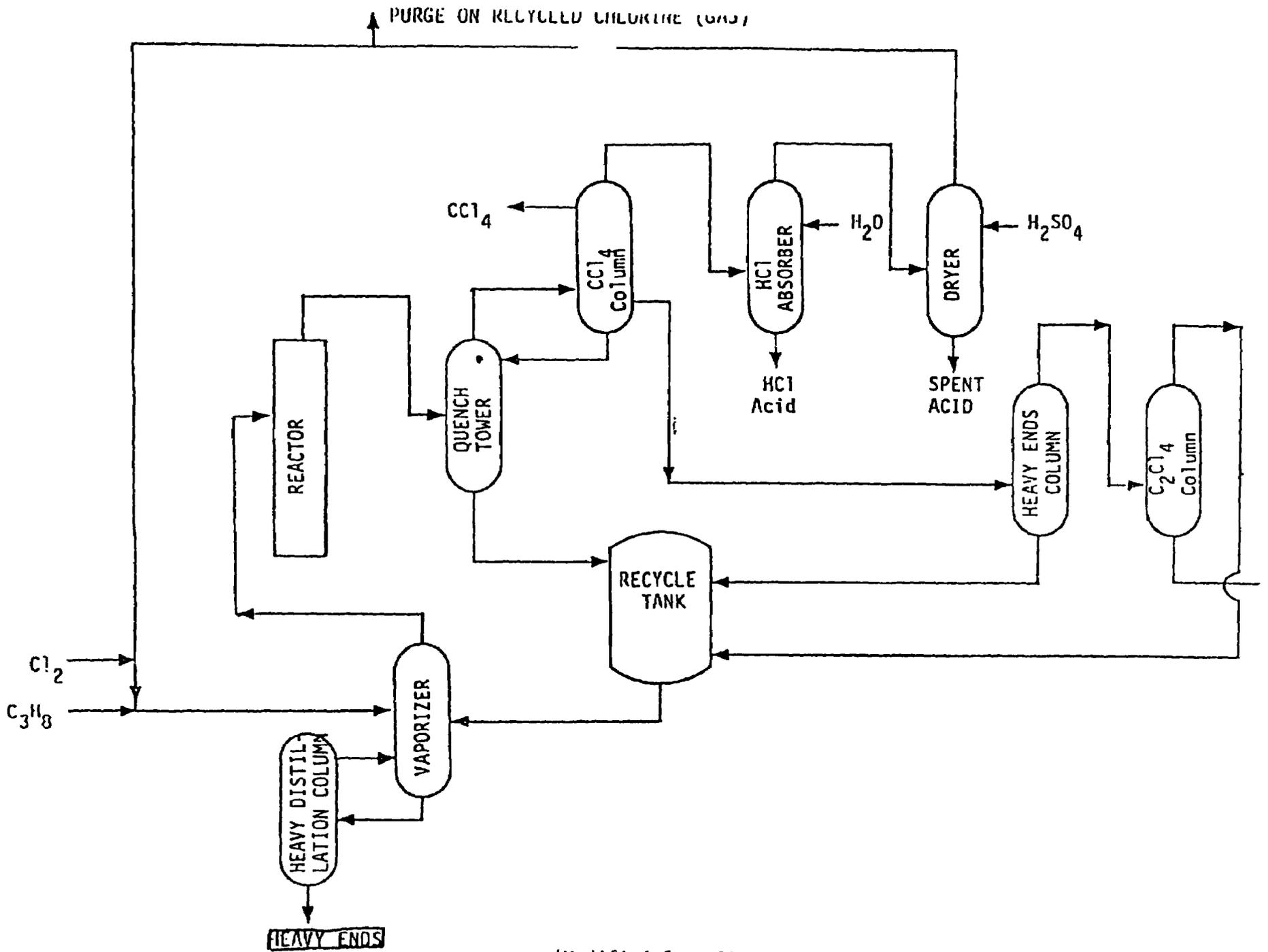


FIGURE 2 \*Modified from 31  
 CARBON TETRACHLORIDE AND PERCHLOROETHYLENE MANUFACTURE VIA Chlorinolysis of Propane

withdrawn. Hydrogen chloride and chlorine are separated and scrubbed with water in a hydrogen chloride absorber to remove HCl as hydrochloric acid by-product. The carbon tetrachloride column returns bottom liquid that is rich in perchloroethene to the heavy ends column. Light ends from this column are recycled to the reactor. In the heavy ends column, the perchloroethylene-rich stream is distilled to remove the heavy ends that are returned for recycle. Overhead from the heavy ends column is fractionated in the perchloroethylene column where the desired quantity of perchlorethylene is removed as bottoms and the overhead, containing largely carbon tetrachloride, is sent to recycle. The final product mix is controlled by the amounts of product recycled to the reactor. Estimated emissions from this process are shown in Table 3.\*

The reaction pathways for these waste constituents are as follows: Hexachloroethane results from the chlorination of product perchloroethylene. Free radical reactions will result in the formation of hexachlorobutadiene (see p. 9 where the reaction chemistry is described). Hexachlorobutadiene could also be formed by chlorination of ethylene radicals under chlorinolysis conditions. Hexachlorobenzene would result from the cyclization and chlorination of C<sub>2</sub> molecules under the high temperature reaction conditions via a Diels-Alder reaction, whereby a cyclic compound is formed from double bond systems.

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\*As presented in Table 3, little or no carbon tetrachloride was recorded found in the air, aqueous and solid emissions. However, based on industry process, this constituent is predicted to be present in the waste. Further, the presence of even very small concentrations of this very potent carcinogen are of concern to the Agency.

TABLE 3

## ESTIMATED EMISSIONS FROM CARBON TETRACHLORIDE MANUFACTURE: Chlorinolysis of Propane

Species	EMISSIONS kg/Mg		
	<u>Air</u>	<u>Aqueous</u>	<u>Solid</u>
Carbon tetrachloride		trace	
Hexachloroethane			trace
Hexachlorobutadiene			3.3
Hexachlorobenzene			3.3
Tars			3.0
Sodium hydroxide		1.1	_____
			10

Source: Elkin, "Chlorinated Solvents," Process Economics Program Report No. 48, Stanford Research Institute, Menlo Park, CA, 1969

b. Chlorinolysis of hexachloroethane with simultaneous chlorination of perchloroethylene (4,2)

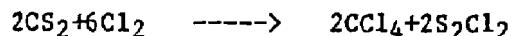
Expected waste constituents of concern from this process (Figure 4) are hexachlorobenzene, hexachlorobutadiene, hexachloroethane, and carbon tetrachloride.\* Some carbon tetrachloride is expected to be present in distillation bottoms since it is the product and would not be completely removed from the bottoms. Hexachloroethane is a feedstock and thus is also expected to be found in the waste. Hexachlorobenzene will result from the cyclization and chlorination of C<sub>2</sub> molecules under high temperature pyrolysis conditions.

The final production process considered is the production of carbon tetrachloride by chlorination of carbon disulfide.

3. Carbon Tetrachloride by Chlorination of Carbon Disulfide (3)

Direct chlorination of carbon disulfide to carbon tetrachloride is a long-established process which, until challenged by chlorination of methane and chlorinolysis of hydrocarbons, was the sole source of carbon tetrachloride. Chlorination of carbon disulfide does have certain advantages: hydrocarbon co-products or by-products and hydrogen chloride are not formed. Because sulfur must be recovered and recycled however, this process is presumed to be integrated with a carbon disulfide production facility.

The overall chemistry of this process is represented by the following equations:



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\*Additional heavy chlorinated hydrocarbons will probably also be present, but their existence is more speculative since they would probably "crack" into lower molecular weight compounds under chlorinolysis conditions.

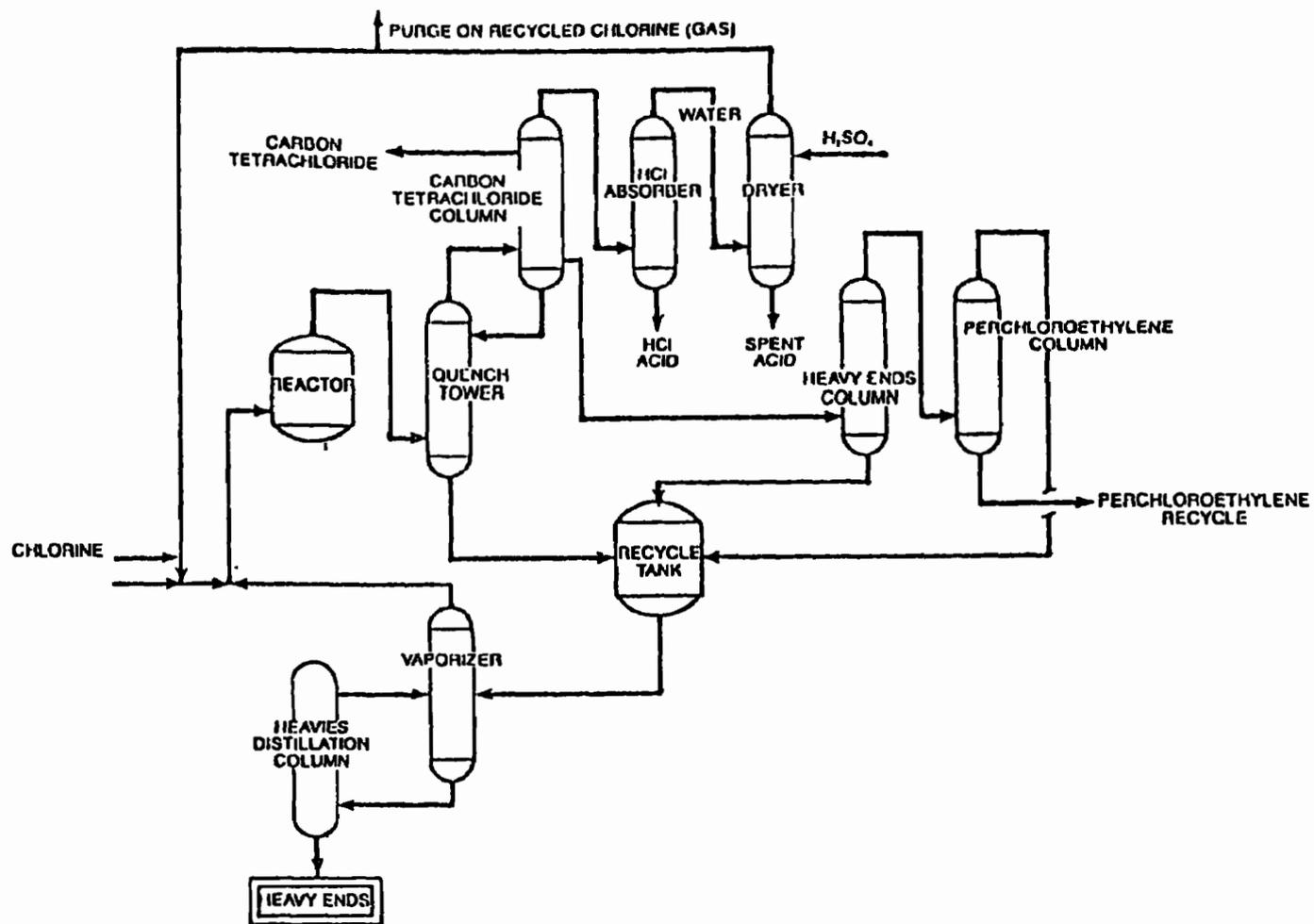


Figure 4. CARBON TETRACHLORIDE BY THE PYROLYSIS OF HEXACHLOROETHANE & PERCHLOROETHYLENE

(Modified from 4,2)

The sulfur monochloride formed reacts with a fresh feed of carbon disulfide to form additional carbon tetrachloride:



This reaction, in contrast to the first reaction, goes only to about 75% completion. The sulfur formed is recycled to carbon disulfide production. Reaction yield is about 95% based on carbon disulfide.

Carbon disulfide, a recycle stream of carbon disulfide/carbon tetrachloride/sulfide monochloride from dechlorination, and chlorine (approx. 1% wt over the stoichiometric requirement) react in the chlorinator at an approximate temperature and pressure of 100°C and 1 atm., respectively. The reaction goes to near completion and the crude product consists principally of carbon tetrachloride and sulfur monochloride, and a small amount of carbon disulfide (>0.1% wt ). Sulfur dichloride formation is minimized by the presence of the carbon disulfide.

The crude product is fractionated into an overhead stream of carbon tetrachloride and a bottom stream of sulfur monochloride and carbon tetrachloride. Chlorine is added to the bottom stream to form small amounts of sulfur dichloride which catalyzes the subsequent dechlorination reaction. The dechlorination reactor operates under reflux conditions using the bottom stream as a feedstock. After dechlorination, the reaction product is separated: the overhead stream ( $CCl_4/CS_2/S_2Cl_2$ ) is recycled to the chlorination reactor; the bottom stream, which is largely sulfur, is purified and recycled to carbon disulfide production. Crude carbon tetrachloride, separated as an overhead stream from the distillation of the chlorination mixture, is washed with either a dilute solution of sodium hydroxide or a suspension of calcium hydroxide to decompose sulfur

monochloride and dichloride. This stream is distilled and water, carbon tetrachloride, and carbon disulfide are removed as an overhead stream. Water is decanted, and the organic layer distilled. The bottom stream from this column is sent to carbon tetrachloride storage.

When properly conducted, this process would probably be waste free. However, if conducted inefficiently, heavy ends could be generated consisting of sulfur monochloride and carbon tetrachloride, probably in equal concentrations. Obviously, the Agency is only listing this process when waste heavy ends are actually generated.

#### C. Waste Generation and Management

The distillation residue waste from the direct chlorination or chlorinolysis of hydrocarbons thus consist of heavy chlorinated hydrocarbons, such as hexachlorobenzene, perchloroethylene, hexachlorobutadiene, carbon tetrachloride, and hexachloroethane. These wastes are generated in large quantities. Based on U.S.I.T.C 1978 production figures of 334,000 metric tons of carbon tetrachloride<sup>(35)</sup> and the waste emission factors set forth above, an estimated 3200 metric tons of waste is generated each year. This estimate may be conservative, since waste emission factors were not calculated for wastes from carbon tetrachloride production by pyrolysis of hexachloroethane. In any case, this is a significant annual quantity of waste generated, and it must further be remembered that this waste will accumulate in greater quantities over time.

Heavy ends from carbon tetrachloride production have typically been disposed of in drums in land disposal facilities, or have been incinerated.<sup>(4)</sup>

### III. Discussion of Basis for Listing

#### A. Hazards Posed by the Waste

The waste constituents of concern, which as shown above are present in these wastes in substantial concentrations, are:

- o Hexachlorobenzene
- o Hexachlorobutadiene
- o Carbon Tetrachloride
- o Hexachloroethane
- o Perchloroethylene

All of these substances except hexachloroethane have been identified by the Agency as being carcinogenic and they are all very toxic. Hexachlorobenzene is also a teratogen. Generation and accumulation of large quantities (over 3000 MT annually, see p. 16) of wastes containing these constituents is itself a reason for imposition of hazardous status. The large quantities of these contaminants pose the danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time, since large amounts of pollutants are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or used up due to the large quantities of pollutant available. All of these considerations increase the possibility of exposure to the harmful constituents in the wastes, and in the Agency's view, support a hazardous listing.

In light of the extreme danger posed by these waste constituents, and the large quantities of waste generated, a decision not to list these waste would be justified, if at all, only if waste constituents were demonstrably unable to migrate and persist. This is not the case, however, since most of these waste constituents have migrated and persisted in actual damage incidents, via both groundwater and air

exposure pathways.

Carbon tetrachloride, for example, has been identified as present in school and basement air at Love Canal, as has hexachlorobutadiene and perchloroethylene . (Source: "Love Canal, Public Health Bomb", a Special Report to the Governor and Legislature, New York State Department of Health, 1978.) Carbon tetrachloride has also been implicated in two groundwater contamination incidents in Plainfield, Connecticut, where drinking water sources were adversely affected (Table 1, Reference 31).

Hexachlorobutadiene, hexachlorobenzene and hexachlorethane also have been shown to migrate from waste disposal sites to groundwater. EPA conducted groundwater monitoring in the vicinity of an (unnamed) chemical waste disposal site in an effort to quantify migrating organic waste constituents. These waste constituents were all found to have migrated (Table 7.2, Reference 31).

Another incident illustrates even more dramatically the migratory potential of these waste constituents. Chemical wastes from Hooker Chemical's disposal sites at Montague, Michigan have migrated from landfills and underground injection wells, moved through and contaminated groundwater supplies, and contaminated a recreational lake. The contaminated plume is 2,000 ft. wide and extends for over 1 mile. Among waste constituents present in the plume are hexachlorobutadiene, hexachlorobenzene and carbon tetrachloride. (31)

Hexachlorobenzene may also pose a hazard through volatilization. A case history of environmental damage in which air, soil, and vege-

tation over an area of 100 square miles was contaminated by hexachlorobenzene (HCB) occurred in 1972.(7) There was volatilization of HCB from landfilled wastes and subsequent bioaccumulation in cattle grazing in the eventually contaminated areas. Accumulation in tissues of cattle occurred, so that the potential risk to humans from eating contaminated meat and other foodstuffs is significant.

These waste constituents thus have proven capable of migration, mobility and persistence, and are demonstrably capable of causing substantial hazard via groundwater, surface water and air exposure routes, if improperly managed. Disposal by incineration is another type of management which could lead to substantial hazard. Improper incineration can result in serious air pollution by the release of toxic fumes occurring when incineration facilities are operated in such a way that combustion is incomplete. In the incineration of wastes containing carbon tetrachloride, phosgene (a highly toxic gas) is likely to be emitted under incomplete combustion conditions.(32,33,34) These conditions can, therefore, result in a significant opportunity for exposure of humans, wildlife and vegetation, in the vicinity of these operations, to potentially harmful substances.

## B. Health and Ecological Effects

### 1. Hexachlorobenzene

Health Effects - Hexachlorobenzene has been found to be carcinogenic in animals.(8,9) It has also been identified by the Agency as a compound which exhibits substantial evidence of being carcinogenic.

This chemical is reportedly teratogenic, known to pass through placental barriers, producing toxic and lethal effects in the fetus.<sup>(10)</sup> Chronic exposure to HCB in rats has been shown to result in damage to the liver and spleen.<sup>(11)</sup> It has been lethal in humans when ingested at one-twentieth the known oral LD<sub>50</sub> dose for rats.<sup>(12)</sup> It has also been demonstrated that at doses far below those which are lethal, HCB enhances the body's capability to toxify rather than detoxify other foreign organic compounds present in the body through its metabolism.<sup>(13)</sup> Hexachlorobenzene is designated a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of hexachlorobenzene can be found in Appendix A.

Ecological Effects - Hexachlorobenzene is likely to contaminate accumulated bottom sediments within surface water systems and bioaccumulate in fish and other aquatic organisms.<sup>(6)</sup>

Regulations - Hexachlorobenzene is a chemical evaluated by CAG as having substantial evidence of carcinogenicity. Ocean dumping of hexachlorobenzene is prohibited. An interim food contamination tolerance of 0.5 ppm has been established by FDA.

Industrial Recognition of Hazard - According to Sax, Dangerous Properties of Industrial Chemicals, HCB is a fire hazard and, when heated, emits toxic fumes.

## 2. Hexachlorobutadiene (HCBd)

Health Effects - Hexachlorobutadiene (HCBd) has been found to be carcinogenic in animals<sup>(14)</sup>. It has also been identified by the

Agency as a compound which exhibits substantial evidence of being carcinogenic. It is an extremely toxic chemical [LD<sub>50</sub> (rat)- 90 mg/kg] via ingestion. Upon chronic exposure of animals in tests conducted by the Dow Chemical Company and others, the kidney appears to be the organ most sensitive to HCBD(14,15,16). Effluents from industrial plants have been found to have HCBD concentrations as high as 240 g/l,(19) more than 200 times the recommended criterion level. HCBD is considered a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of hexachlorobutadiene can be found in Appendix A.

Ecological Effects - HCBD is likely to contaminate accumulated bottom sediments within surface water systems and is likely to bioaccumulate in fish and other aquatic organisms(6).

The USEPA (1979) has estimated the BCF at 870 for the edible portion of fish and shellfish consumed by Americans. Hexachlorobutadiene is persistent in the environment(18).

Industrial Recognition of Hazard - Hexachlorobutadiene is considered to have a high toxic hazard rating via both oral and inhalation routes (Sax, Dangerous Properties of Industrial Materials).

### 3. Carbon Tetrachloride

Health Effects - Carbon tetrachloride is a very potent carcinogen(19) and has been identified by the Agency as a compound which exhibits substantial evidence of being carcinogenic. It has also been shown to be teratogenic in rats when inhaled at low concentrations.(20)

Chronic effects of this chemical in the human central nervous system have occurred following inhalation of extremely low concentrations [20 ppm]<sup>(21)</sup> with death at 1000 ppm.<sup>(22)</sup> Adverse effects of carbon tetrachloride on liver and kidney functions<sup>(23)</sup> and on respiratory and gastrointestinal tracts<sup>(23,24)</sup> have also been reported. Death has been caused in humans through small doses.<sup>(25)</sup> The toxic effects of carbon tetrachloride are amplified by both the habitual and occasional ingestion of alcohol.<sup>(26)</sup> Especially sensitive to the toxic effects of carbon tetrachloride are obese individuals because the compound accumulates in body fat.<sup>(16)</sup> It also causes harmful effects in undernourished humans, those suffering from pulmonary diseases, gastric ulcers, liver or kidney diseases, diabetes, or glandular disturbances.<sup>(27)</sup> Carbon tetrachloride is a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of carbon tetrachloride can be found in Appendix A.

Ecological Effects - In measurements made during the National Organics Monitoring Survey of 113 public water systems sampled, 11 of these systems had carbon tetrachloride at levels at or exceeding the recommended safe limit.<sup>(28)</sup>

Regulations - OSHA has set a TWA for carbon tetrachloride at 10 ppm. Carbon tetrachloride has been banned under the Hazardous Substances Act by the Consumer Product Safety Commission.

Industrial Recognition of Hazard - According to Sax, Dangerous Properties of Industrial Materials, carbon tetrachloride is considered a high systemic poison through ingestion and inhalation.

#### 4. Hexachloroethane

Health Effects - Hexachloroethane has been reported to be carcinogenic to animals, meaning that humans may be similarly affected(25). Humans exposed to vapors at low concentrations for long periods have had liver, kidney and heart degeneration and central nervous system damage(26). Hexachloroethane is slightly toxic via ingestion. It is a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of hexachloroethane can be found in Appendix A.

Regulations - OSHA has set a TWA for hexachloroethane at 1 ppm (skin).

Industrial Recognition of Hazard - According to Sax, Dangerous Properties of Industrial Materials, hexachloroethane has a moderate toxic hazard rating.

#### 5. Perchloroethylene (Tetrachloroethylene)

Health Effects - Perchloroethylene (PCE) was reported carcinogenic to mice (36). It has also been identified by the Agency as a compound which exhibits substantial evidence of being carcinogenic. PCE is chronically toxic to rats and mice, causing kidney and liver damage (36,37,38), and to humans, causing impaired liver function (39). Subjective central nervous system complaints were noted in workers occupationally exposed to PCE (40). PCE is also reported acutely toxic in varying degrees to several fresh and salt water organisms, and chronically toxic to salt water organisms (41,42).

#### IV. References

1. Not used in text
2. Kirk Othmer. Encyclopedia of chemical technology. 2d ed. New York. Interscience Publishers, New York. 1963.
3. Stanford Research Institute. 1979 Directory of chemical producers - U.S.A. SRI International, Menlo Park, CA. 1979.
4. Kahn, Z.S., and T.W. Hughes. Source Assessment: Chlorinated hydrocarbons. EPA No. 600/2-79-019g. August, 1979.
5. Not used in text.
6. U.S. EPA. Technical support document for aquatic fate and transport estimates for hazardous chemical exposure assessments. U.S. EPA Environmental Research Lab., Athens, GA. 1980.
7. U.S. EPA. Hazardous waste disposal reports. No. 3. EPA No. 530/SW 151.3. 1976.
8. Cabral, J. R. P., et al. Carcinogenic activity of hexachlorobenzene in hamsters. Tox. Appl. Pharmacol. 41:155. 1977.
9. Cabral, J. R. P., et al. Carcinogenesis study in mice with hexachlorobenzene. Toxicol. Appl. Pharmacol. 45:323. 1978.
10. Grant, D. L., et al. Effect of hexachlorobenzene on reproduction in the rat. Arch. Environ. Contam. Toxicol. 5:207. 1977.
11. Koss, G., et al. Studies on the toxicology of hexachlorobenzene. III. Observations in a long-term experiment. Arch. Toxicol. 40:285. 1978.
12. Gleason, M.N., et al. Clinical toxicology of commercial products - Acute poisoning. 3rd ed., p. 76. 1969.
13. Carlson, G. P. Induction of cytochrome P-450 by halogenated benzenes. Biochem. Pharmacol. 27:361. 1978.
14. Kociba et al. Toxicologic study of female rats administered hexachlorobutadiene or hexachlorobenzene for 30 days. Dow Chemical Company. 1971.
15. Kociba, R.J. Results of a two-year chronic toxicity study with hexachlorobutadiene in rats. Amer. Ind. Hyg. Assoc. 38:589. 1977.
16. Schwetz, et. al. Results of a reproduction study in rats fed diets containing hexachlorobutadiene. Toxicol. Appl. Pharmacol. 42:387. 1977.

17. Not used in text.
18. U.S. EPA. Water-related environmental fate of 129 priority pollutants. EPA No. 440/4-79-029b. 1979.
19. IARC Monographs on the evaluation of carcinogenic risk of chemicals to man. V. I and V. XX. World Health Organization. 1972.
20. Schwetz, B. A., B. K. J. Leong and P. H. Gehring. Embryo- and fetotoxicity of inhaled carbon tetrachloride, 1,1-dichloroethane and methyl ethyl ketone in rats. Toxicol. Appl. Pharmacol. 28(3):452-464. 1974.
21. Elkins, Harvey B. The chemistry of industrial toxicology. 2nd ed. John Wiley & Sons, New York. p. 136. 1966.
22. Association of American Pesticide Control Officials, Inc. Pesticide chemical official compendium. 1966.
23. Texas Medical Association. Texas Medicine 69:86. 1973.
24. Davis, Paul A. Carbon tetrachloride as an industrial hazard. JAMA 103:962-966. 1934.
25. Dreisbach, Robert H. Handbook of poisoning: Diagnosis and treatment, 8th ed. Lange Medical Publications, Los Altos, CA. p. 128. 1974.
26. U.S. EPA. Carbon tetrachloride: Ambient water quality criteria document. NTIS PB No. 292 424. 1979.
27. Von Oettingen, W.F. The halogenated hydrocarbons of industrial and toxicological importance. In: Elsevier monographs on toxic agents. E. Browning, ed. Elsevier Publishing Co., NY. 1964.
28. U.S. EPA. The National Organic Monitoring Survey. Technical Support Division, Office of Water Supply, U.S. EPA. Washington, DC. 20460. 1978.
29. Not used in text.
30. Not used in text.
31. Accurex Corp. Preliminary draft report: Chlorinated hydrocarbon manufacture: An overview. Contract No. 68-02-2567. February 29, 1980.
32. Edward, J.B. Combustion formation and emission of trace species. Ann Arbor Science. 1977.

33. NIOSH. Criteria for recommended standard: Occupational exposure to phosgene. HEW, PHS, CDC, NIOSH. 1976.
34. Chemical and Process Technology Encyclopedia. McGraw Hill. 1974.
35. U.S. International Trade Commission. Synthetic Organic Chemical. 1979.
36. National Cancer Institute. Bioassay of tetrachloroethylene for possible carcinogenicity. CAS No. 177-18-4. Nc I-C6-TR-13. DHEW Publication No.(NIH) 77-813. NTIS PB No. 272 940. 1977.
37. Rowe, V.K., et al. Vapor toxicity of tetrachloroethylene for laboratory animal and human subjects. AMA Arch. Ind. Hyg. Occup. Med. 5:566. 1952.
38. Klaasen, C.D., and G.L. Plaa. Relative effects of chlorinated hydrocarbons on liver and kidney function in dogs. Toxicol. Appl. Pharmacol. 10:119. 1967.
39. Coler, H. R., and H. R. Rossmiller. Tetrachloroethylene exposure in a small industry. Ind. Hyg. Med. 8:227. 1953.
40. Medek, V., and J. Kavarik. The effects of perchloroethylene on the health of workers. Pracovní Lekarství. 25:339. 1973.
41. U. S. EPA. In-depth studies on health and environmental impacts of selected water pollutants. Contract No. 68-01-4646. 1978.
42. U. S. EPA. Tetrachloroethylene: Ambient water quality criteria NTIS PB No. 292 445. 1979.

Response to Comments - Heavy Ends or Distillation Residues from  
the Production of Carbon Tetrachloride

One commenter requested that the Agency reassess its interpretation of what materials actually constitute waste in the production of carbon tetrachloride. The commenter pointed out that many of these materials are not discarded and never become wastes; that instead, they are further processed within a short time to other products and manufacturing intermediates.

In reviewing the available information, the Agency has evidence to indicate that these wastes have typically been disposed of in drums in land disposal facilities, or have been incinerated. Therefore, these wastes are "discarded and, thus, meet the definition of a solid waste (§261.2) and will continue to be listed as hazardous. However, this waste is not always discarded, as evidenced by the comments received (i.e., these wastes may be used, reused, recycled or reclaimed). As discussed in the preamble to the Part 261 regulations promulgated on May 19, 1980 (45 FR 33091 - 33095), the Agency has concluded that it does have jurisdiction under Subtitle C of RCRA to regulate waste materials that are used, reused, recycled or reclaimed. A large number of comments have been received, however, which challenge this conclusion. The Agency is giving these comments serious consideration but has not presently finalized this portion of the regulations. Therefore, until a final decision is reached with respect to materials which are used, reused, recycled or reclaimed, the following guidance is offered to individual plants to assist them in determining

their responsibilities under the hazardous waste regulations:

- ° If the listed waste is always discarded at the individual plant, the waste is always subject to the full set of hazardous waste regulations.
- ° If the listed waste is sometimes discarded at a particular plant, but is sometimes used, reused, recycled or reclaimed, (not used as an intermediate), the waste would only be subject to the full set of hazardous waste regulations when discarded. When used, reused, recycled or reclaimed the waste would be subject to the special requirements for listed wastes contained in §261.6(b) of the hazardous waste regulations (45 FR 33120).
- ° If the listed waste is typically processed through the next step of the process within a short time, the material does not meet the definition of a solid waste, i.e., is an intermediate product, and is therefore not subject to the hazardous waste regulations (45 FR 33119, and see discussion at 45 FR 33093-33094).

## LISTING BACKGROUND DOCUMENT

## EPICHLOROHYDRIN PRODUCTION

Heavy ends (still bottoms) from the purification column in the production of epichlorohydrin. (T)

I. Summary of Basis for Listing

Heavy ends from the fractionator column in the production of epichlorohydrin contain carcinogens, mutagens, and toxic organic substances. These include epichlorohydrin, trichloropropane and dichloropropanol, and the chloroethers, as pollutants of concern.

The Administrator has determined that the solid waste from epichlorohydrin production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. The heavy ends from the production of epichlorohydrin contain epichlorohydrin and chloroethers which have been identified by EPA's Cancer Assessment Group as substances exhibiting substantial evidence of carcinogenicity. These compounds have also been reported in the literature to show mutagenic potential. The waste also contains trichloropropane and dichloropropanols which are very toxic.
2. Approximately 12,500 tons of the heavy bottoms were generated in 1978 by two manufacturers at three locations along the Gulf Coast.
3. The heavy wastes are stored in holding ponds prior to incineration; during storage there is the potential for ground and surface water contamination by leaching. Epichlorohydrin in the waste also would tend to volatilize and could present an air pollution hazard. If incineration

is incomplete, airborne dispersion of hazardous vapors presents a potential of human risk.

4. Incidents of epichlorohydrin contamination of water supplies have occurred.

## II. Sources of Wastes and Typical Disposal Practices

### A. Industry Profile

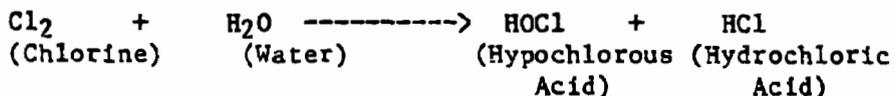
Epichlorohydrin is manufactured by Dow, U.S.A. at Freeport, Tex. and by Shell Chemical Co. at Deer Park, Tex., and Norco, La. (25) The capacities of these plants range from 55 to 275 million pounds per year. About 470 million pounds of epichlorohydrin were produced in 1978. (26,27)

Epichlorohydrin is used mainly as an intermediate for the manufacture of glycerin and epoxy resins. (25) It is also used in the manufacture of plasticizers, surfactants, stabilizers, and ion exchange resins. (25) Growth is expected at 6 to 7% per year. (25)

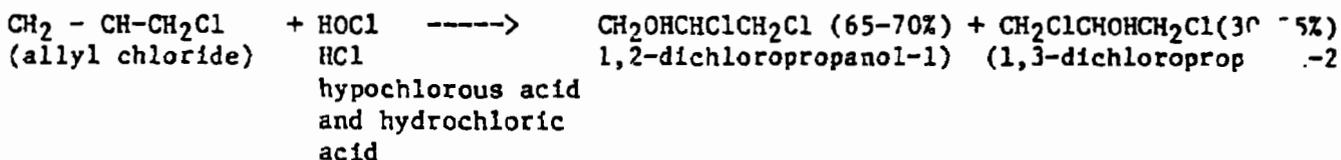
### B. Manufacturing Process

Epichlorohydrin is produced by the following reaction sequence:

Step 1:



Step 2:





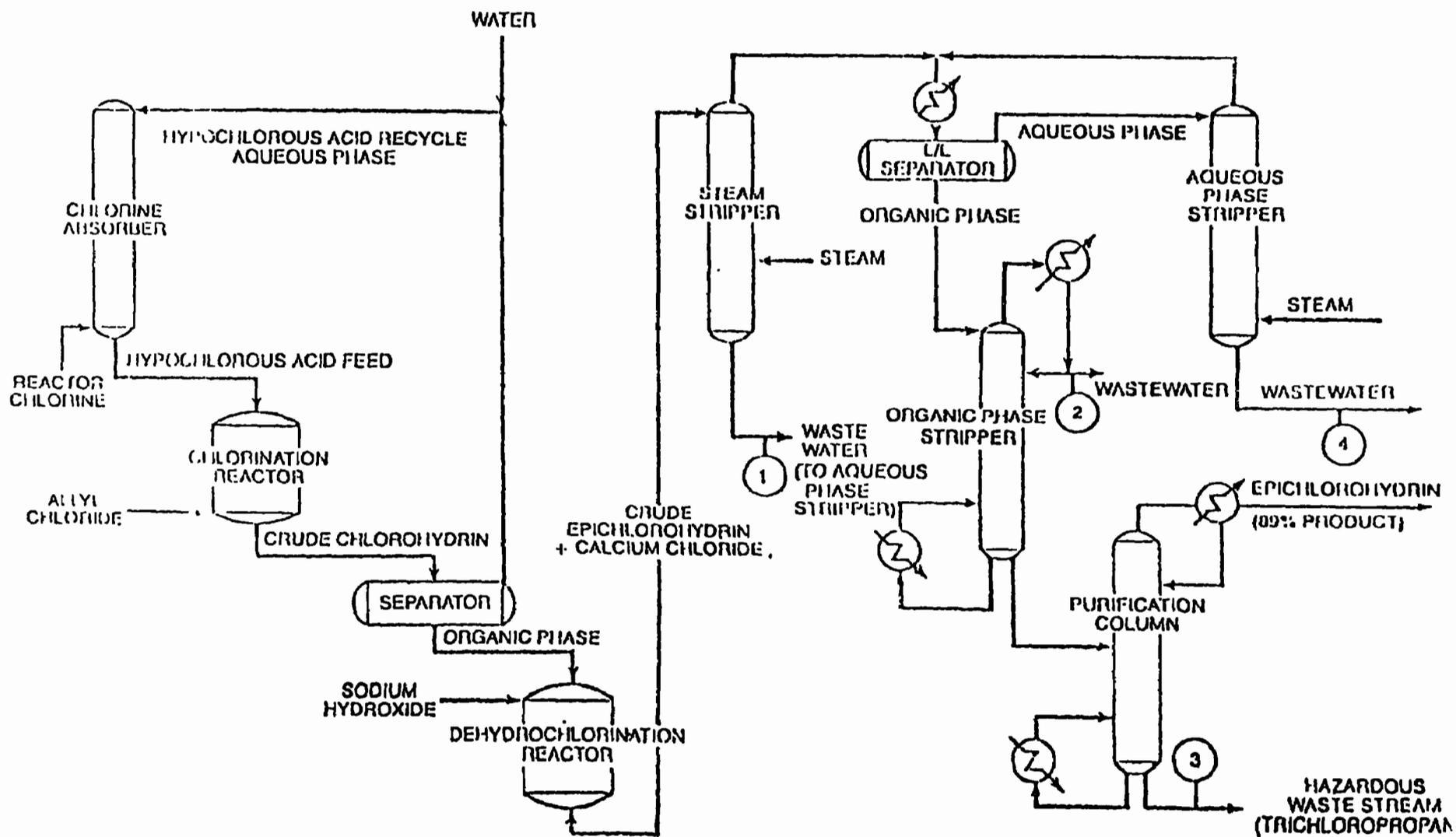


Figure 1: EPICHLOROHYDRIN FROM ALLYL CHLORIDE VIA DEHYDROCHLORINATION OF DICHLOROHYDRINS

The waste water from the bottom of the steam stripper<sup>(1)</sup> is stripped in the aqueous phase stripper where small amounts of epichlorohydrin are recovered overhead and recycled to the steam-stripper condenser; the bottom stream is discharged as water waste.\*

The bottom organic phase from the liquid/liquid separator is fed to the organic phase stripper where residual water is removed overhead.<sup>(2)</sup> The bottom stream of crude epichlorohydrin is fed to the purification column where it is purified by fractionation<sup>(3)</sup> Purified epichlorohydrin is distilled overhead. The bottom stream from the purification column is the waste stream of concern in this document.

#### C. Waste Generation and Management

The waste stream from this process is the heavy organic bottoms (stream 3) from the product purification column. Three plants (two in Texas, one in Louisiana) generated 12,500 tons of heavy ends (still bottoms) in the production of 469.6 million lbs. of epichlorohydrin in 1978<sup>(26,27)</sup>. The primary disposal technique (1979) was reported to be incineration. It is assumed, based on usual waste management practice, that the heavy ends are stored in holding ponds or other temporary storage facilities prior to incineration.

### III. Discussion of Basis for listing

#### A. Hazards Posed by the Waste

Epichlorohydrin purification column bottoms typically contain the following contaminants in the indicated concentrations:<sup>(27)</sup>

\*This water stream is not presently listed as hazardous.

	<u>Percent</u>
Epichlorohydrin	2
Chloroethers	14
Trichloropropane	70
Dichloropropanol	10
Chlorinated aliphatics	<u>4</u>
	100

The waste constituents of concern are epichlorohydrin, the chloroethers, trichloropropane and dichloropropanol. Epichlorohydrin has been identified as a substance exhibiting substantial evidence of carcinogenicity by EPA's Carcinogen Assessment Group. It is also an animal mutagen and is very toxic. The chloroethers are likewise recognized by the Agency as known animal and likely human carcinogens. Their toxicity is likewise high. (See pp. 9-13 following.) Trichloropropane and dichloropropanol are very toxic. Large quantities are therefore available for environmental release in high concentrations.

These waste constituents are present in very substantial concentrations and are generated in large quantities (12,500 tons in 1978). There is thus a strong likelihood that the waste constituents will reach environmental receptors and cause substantial hazard if waste constituents are mismanaged.

Waste mismanagement may certainly occur. As noted above, the primary disposal for this waste is by incineration prior to which the waste may be stored in holding ponds or other temporary storage containers. Disposal by incineration, if mismanaged, could result in serious air pollution through release of toxic fumes. This may occur when incineration facilities are operated in such a way that combustion is incomplete (i.e. inadequate conditions of temperature, mixing and residence time) resulting in airborne dispersion of hazardous vapors containing waste constituents of concern, as well as other newly formed harmful organic substances. Phosgene is an example of a partially combusted chlorinated organic which is produced by the decomposition of chlorinated organics by heat.(32,33,34) This could present a significant opportunity for exposure of humans, wildlife and vegetation in the vicinity of these operations to risk through direct contact and also through pollution of surface waters.

Temporary storage, if not properly managed, may also lead to the release of harmful constituents. Thus, if holding ponds lack proper flood control design features, there is a danger that the organics, during periods of heavy precipitation could be emitted due to flooding of the ponds. Should flooding occur, epichlorohydrin is stable enough to be transported to surface waters. (Appendix B) This eventually could result in drinking water contamination. Actual contamination of

a public water supply by epichlorohydrin occurred on January 23, 1978, when a tank car derailed, spilling 197,000 pounds of epichlorohydrin in West Virginia.\* Nearby wells at a depth of 25 feet were heavily contaminated, demonstrating ability to be mobile in soils. A similar hazard could result if epichlorohydrin-containing wastes were disposed in an uncontrolled pond or lagoon.

The chloroethers are also capable of significant migration via surface water pathways.<sup>(4)</sup> They have been found in surface and groundwaters at concentrations exceeding the USEPA recommended maximum allowable concentration levels in drinking water of 0.42mg/l, demonstrating a propensity to migrate and persist.<sup>(6)\*\*</sup>

Waste constituents might also escape from the holding pond via a groundwater pathway if storage is improper (for instance using ponds in locations with permeable soils). Epichlorohydrin is highly soluble (66,000 ppm), and is thus capable of migration. It adsorbs to organic constituents in soil, and so mobility would be high where organic content is low.<sup>(28)</sup> The chloroethers are also highly soluble (Appendix B) and, although tending to adsorb to soils, have been shown to be mobile and persistent enough to be found in groundwater at concentrations exceeding the proposed human health water quality criteria, as noted above.\*\*

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\* OSW Hazardous Waste Division, Hazardous Waste Incidents, unpublished, open file, 1978.

\*\* The Agency is not using these standards as quantitative benchmarks, but is citing them to give some indication that very low concentrations of these contaminants may give rise to substantial hazard.

From the holding ponds or in surface water, most of the chlorinated propanols would undergo hydrolysis and biodegradation. The dissolved portion, however, could move with a water front through the soil profile. Under some conditions, the chlorinated propanols could reach a ground water aquifer (Appendix B). Degradation of chlorinated propanols in groundwaters would be much slower as evidenced by the observance of many related chlorinated ethanes, ethylenes, in Love Canal leachate, methanol, ethanol and isopropyl alcohol some 30 years after disposal. (29,30,31)

Data show that chemical analogs, dichloroethane<sup>(7)</sup> and dibromochloropropane,<sup>(8)</sup> have permeated the soil mantle to contaminate groundwater, again suggesting a similar behavior for propanols. In addition the chloropropanols tend to bioaccumulate in aquatic organisms,<sup>(9)</sup> thus increasing potential exposure to higher levels of the food chain, including man.

Epichlorohydrin could also pose a threat via an inhalation exposure pathway due to its relatively high volatility. (28) Thus, lack of adequate cover could result in air pollution to surrounding areas.

B. Health and Ecological Effects

1. Epichlorohydrin

Health Effects - Epichlorohydrin has been demonstrated to be carcinogenic in animals<sup>(1)</sup> upon inhalation of vapors. This compound has also been recognized by the Agency as a chemical compound which has exhibited substantial evidence of carcinogenicity. <sup>(35)</sup> Epichlorohydrin is very toxic [oral rat LD<sub>50</sub>=90mg/Kg]. Both respiratory cancers and leukemia are in excess among some exposed worker populations.<sup>(10,11)</sup> Epichlorohydrin vapor also has been demonstrated to induce aberrations in humans and animal chromosomes<sup>(12,13)</sup> and has induced birth defects in animal studies conducted by the Dow Chemical Company. It is a known mutagen to non-mammalian species.<sup>(7)</sup> Several investigators have found that epichlorohydrin possesses anti-fertility properties<sup>(10)</sup>. Altered reproductive function has been reported for workers occupationally exposed to epichlorohydrin. Dow Chemical Company researchers have observed degenerative changes in nasal tissue; severe kidney and liver damage has also been found in animals exposed to vapors of epichlorohydrin.<sup>(16,17)</sup> Additional information and specific references on the adverse effects of epichlorohydrin can be found in Appendix A.

Regulatory Recognition of Hazards - The OSHA time weighted average for skin contact with epichlorohydrin in air is 5 ppm. DOT requires a label warning that this chemical is a poison and a flammable liquid.

Industrial Recognition of Hazards - Epichlorohydrin is intensely irritating and moderately toxic by the oral, percutaneous and subcutaneous routes as well as by inhalation of the vapors (Fassett and Irish, Industrial Hygiene and Toxicology). Plunkett considers it highly toxic in his Handbook of Industrial Toxicology.

2. Chloroethers - bis (chloromethyl) ether and bis (2-chloroethyl) ethers

Health Effects Both bis (chloromethyl) ether and bis (2-chloroethyl) ethers are identified as carcinogens in animals(18,19) under laboratory conditions. These chemicals have also been recognized by the Agency as demonstrating substantial evidence of carcinogenicity. Bis (chloromethyl) ether is very toxic [oral rat LD<sub>50</sub>=210 mg/Kg; inhalation rat LD<sub>50</sub>=7ppm/7h]. Bis (2chloroethyl) ether is also very toxic (oral rat LD<sub>50</sub>=75mg/Kg). Epidemiological studies of workers in the United States, Germany and Japan who were occupationally exposed to both ethers indicate that they are human carcinogens.(20) They have also been shown to be mutagens in bacterial screening systems.(20) Additional information and specific references on the adverse effects of chloroethers can be found in Appendix A.

Regulatory Recognition of Hazard - Chloroethers are designated as priority pollutants under Section 307(a) of the CWA. Bis (chloroethyl) ether has a designated OSHA ceiling of 15 ppm. Bis (chloromethyl) ether is designated by OSHA as a carcinogen and is required by DOT to carry labels that say "flammable liquid" and "poison".

Industrial Recognition of Hazard - Sax (Dangerous Properties of Industrial Materials) states that bis (chloromethyl) ether has an unknown systemic toxic hazard rating but it is a carcinogen. Bis 2 (chloroethyl) ether is highly toxic via ingestion, inhalation and skin absorption. Both chemicals are listed as priority pollutants by the EPA.

3. Trichloropropane

Health Effects - 1,2,3-Trichloropropane is a strong irritant and can be toxic by oral ingestion, inhalation, or dermal application.<sup>(21,22)</sup> Trichloropropane is very toxic [oral rat LD<sub>50</sub>=320 mg/Kg]. Tsulaya et al<sup>(23)</sup> observed significant changes in central nervous system function, as well as enzyme changes in blood, liver, and lungs. Additional information and specific references on the adverse effect of trichloropropane can be found in Appendix A.

Regulations - The OSHA TWA for trichloropropane in air is 50 ppm.

Industrial Recognition of Hazard - Trichloropropane is designated in Sax, Dangerous Properties of Industrial Materials, as a highly toxic skin irritant, moderately toxic systemic poison via oral, inhalation and skin absorption routes and as a cumulative toxin.

4. Dichloropropanols

Health Effects - Both industrially occurring isomers, 1,3-dichloropropanol-2 [oral rat LD<sub>50</sub>=90 mg/Kg] and 1,2-dichloropropanol-3 [oral rat LD<sub>50</sub>=490 mg/Kg] are very toxic to laboratory animals, causing systemic as well as local toxic effects. The toxic symptoms caused by the 1,3 isomer have

been compared to that of the liver toxin carbon tetrachloride which causes acute and often irreversible hepatic failure. Both compounds are potent skin and lung irritants, absorbed by all routes of exposure and tend to accumulate in the organism.(24) Additional information and specific references on the adverse effects of dichloropropanols can be found in Appendix A.

Industrial Recognition of Hazard - Dichloropropanol is designated in Sax, Dangerous Properties of Industrial Materials as moderately toxic via inhalation and highly toxic via ingestion(24).

#### IV. References

1. Nelson, N. Communication to the regulatory agencies of preliminary findings of a carcinogenic effect in the nasal cavity of rats exposed to epichlorohydrin. New York University Medical Center, letter dated 28 March 1977.
2. Nelson, N. Updated communication to the regulatory agencies of preliminary findings of a carcinogenic effect in the nasal cavity of rats exposed to epichlorohydrin. New York University Medical Center, letter dated 23 June 1978.
3. Peterson, C.A., Jr. Emission control options for the synthetic organic chemicals manufacturing industry. Glycerin and its intermediates. Abbreviated product report. EPA Contract No. 68-02-2577. March, 1979.
4. Zoeteman, B. C. J., et al. Persistent organic pollutants in river water and groundwater of the Netherlands. In: Proceedings; 3rd Int'l Symposium on Aquatic Pollutants. Jekyll Island, GA. October 15-17, 1979.
5. Not used in text.
6. U.S. EPA. Preliminary assessment of suspected carcinogens in drinking water. Report to Congress. EPA No. 560/4-75-003. U.S. EPA. Washington, DC. 20460. 1975.
7. De Walle, F. P., and E.S.K. Chian. Detection of trace organics in well water near a solid waste landfill. In Proceedings: 34th Industrial Waste Conference. Lafayette. May 8-10, 1979. Purdue University. Ann Arbor Science p. 742-52. 1980.
8. Weisser, P. News Release, Department of Health Services. Sacramento, CA. August 23, 1979.
9. Clement Associates, Inc. Dossier on chloropropanes (Draft). Contract No. EABAC013, prepared for TSCA Interagency Testing Committee. Washington, D.C. August, 1978.
10. Enterline, P. E. Mortality experience of workers exposed to epichlorohydrin. In press: Jour. Occup. Medicine. 1979.
11. Enterline, P. E., and V. L. Henderson. Communication to Medical Director of the Shell Oil Company: Preliminary finding of the updated mortality study among workers exposed to epichlorohydrin. Letter dated July 31, 1978. Distributed to Document Control Office, Office of Toxic Substances, WH-557. U.S. EPA. 1978.
12. Syracuse Research Corporation. Summarization of recent literature pertaining to an occupational health standard for epichlorohydrin. Report prepared by Syracuse Research Corporation for NIOSH. 1980.

IV. References (Continued)

13. Santodonato, et al. Investigation of selected potential environmental contaminants: Epichlorohydrin and epibromohydrin. Syracuse Research Corporation. Prepared for the Office of Toxic Substances, US. EPA. EPA No. 560/11-80-006. NTIS PB No. 197 585. 1979.
14. Not used in text.
15. Not used in text.
16. Quast, J. F. et al. Epichlorohydrin - subchronic studies I. A 90-day inhalation study in laboratory rodents. Unpublished report from Dow Chemical Company, Freeport, Texas. January 12, 1979.
17. Quast, J. F. et al. Epichlorohydrin - subchronic studies. I. A 12-day study in laboratory rodents. Unpublished report from Dow Chemical Company, Freeport, Texas. January 12, 1979.
18. Innes, et al. Bioassay of pesticides and industrial chemicals for tumorigenicity in mice, a preliminary note. J. Natl. Cancer Inst. 42:1101. 1969.
19. Juschner, et al. Inhalation carcinogenicity of alpha haloethers III. Lifetime and limited period inhalation studies with bis(chloromethyl) ether at 0.1 ppm. Archives of Environmental Health 30:73. 1975.
20. U.S. EPA. Chloroalkyl ethers: Ambient water quality criteria. NTIS PB No. 297 921. 1979.
21. Hawley, G. G. Condensed chemical dictionary, 9th ed. Van Nostrand Reinhold Co., New York. 1977.
22. NIOSH. Registry of toxic effects of chemical substances. U.S. DHEW, PHS, CDC, DHEW (NIOSH) No. 78-104-A and No. 78-104-B. 1978.
23. Tsulaya, V. R., et al. Toxicology features of certain chlorine derivatives of hydrocarbons. Gig. Sanit. 8:50-53. 1977.
24. Sax, N. I. Dangerous properties of industrial materials, 5th ed. Van Nostrand Reinhold Co., New York. 1979.
25. Kirk-Othmer. Encyclopedia of chemical technology. 2nd ed. V.I. John Wiley and Sons, New York. 1970.
26. Peterson, C. A. Emission control options for the synthetic organic chemicals manufacturing industry: Glycerin and its intermediates. Abbreviated product report. EPA Contract No. 68-02-2577. March, 1979.

27. U.S. EPA. Assessment of industrial hazardous waste practices: Organic chemicals, pesticides and explosives industries. EPA No. SW 118c. p. 5-20. NTIS PB No. 251 307. January, 1976.
28. Dawson, English and Petty. Physical chemical properties of hazardous waste constituents. 1980.
29. Barth, E.F., and Cohen, J.M. Evaluation of treatability of industrial landfill leachate. Unpublished report. U.S. EPA. Cincinnati, Ohio. November, 1978.
30. O'Brien, R.P. City of Niagara Falls, N.Y., Love Canal Project. Unpublished Report. Calgon Corp. Calgon Environmental Systems Division. Pittsburgh, Pa.
31. RCERA Research, Inc. Priority pollutant analyses prepared for NUCO Chemical Waste Systems, Inc. Unpublished report. Tonawanda, N.Y. 1979.
32. Edwards, John B. Combustion formation and emission of trace species. Ann Arbor Science. 1977.
33. NIOSH Criteria for recommended standard: Occupational exposure to phosgene. HEW, PHS, CDC, NIOSH. NTIS PB No. 267 514. 1976.
34. Chemical and process technology encyclopedia. McGraw Hill. 1974.
35. U.S. EPA. Office of Research and Development. Carcinogen Assessment Group. List of Carcinogens. April 22, 1980.

Response to Comments - Heavy Ends (Still Bottoms) from  
the Purification Column in the Production of Epichlorohydrin

Heavy ends (still bottoms) from the purification column in the production of epichlorohydrin (K017) are listed as hazardous because they contain a number of toxic constituents, including epichlorohydrin. One commenter objected to the inclusion of epichlorohydrin as a constituent of concern in this particular listing. The commenter argued that since there are only two manufacturers at a total of only three sites in the U.S., the likelihood that the waste constituents, especially epichlorohydrin, will reach environmental receptors and cause substantial hazard is small especially since the commenter believes that epichlorohydrin is "readily degradable" (i.e., the commenter believes that the statement in the listing background document that "epichlorohydrin is stable enough to be transported to surface waters" (EPA BD-11 at 302) is unsupported by the absence of any hydrolysis rates, microbial degradation rates, photolysis rates or oxidation rates). Further, the commenter believes that the Agency may have misinterpreted the toxicological studies of epichlorohydrin conducted by the Dow Chemical Co. The commenter therefore recommends that epichlorohydrin be deleted as a basis for listing waste K017.

The Agency strongly disagrees with the commenter's unsubstantiated conclusion. While manufactured at only three sites, these plants are all located on the Texas/Louisiana

Gulf Coast area where the average yearly rainfall is heavy and the groundwater is close to the surface. The waste constituents, including epichlorohydrin, are also present in substantial concentrations and are generated in large quantities. Therefore, should the large amounts of waste constituents be exposed to a leaching media and be released as a result of mismanagement, large areas of ground and surface waters may be affected in the Texas/Louisiana Gulf Coast area. Additionally, while information may be limited on hydrolysis rates, microbial degradation rates, photolysis rates and oxidation rates, epichlorohydrin has in fact been documented to migrate and contaminate drinking water. Further, as noted in the background document, the primary disposal for this waste is by incineration prior to which the waste may be stored in holding ponds or other temporary storage containers. Disposal by incineration, if mismanaged, could result in the release of toxic fumes when incineration facilities are operated in such a way that combustion is incomplete; phosgene is an example of a partially combusted chlorinated organic which is produced by the decomposition of chlorinated organics by heat.

Finally, the Agency, in assessing the toxicity/carcinogenicity of epichlorohydrin, used a number of studies, including some conducted by the Dow Chemical Co. in arriving at the conclusion that epichlorohydrin is toxic/carcinogenic. In fact, before a chemical compound is deemed carcinogenic

by CAG, it is subject to much detailed study of the literature, thus, is unlikely that the Agency has misinterpreted the commenter's data. The Agency, therefore, will continue to include epichlorohydrin as a constituent of concern in this particular listing.

## LISTING BACKGROUND DOCUMENTS

## ETHYL CHLORIDE PRODUCTION

## Heavy Ends from the Fractionation Column in Ethyl Chloride Production (T)

I. SUMMARY OF BASIS FOR LISTING

The heavy ends or bottoms from the fractionation column used in the production of ethyl chloride contains 1,2-dichloroethane, trichloroethylene and many other heavy chlorinated organics. The Administrator has determined that these sludges are solid wastes which may pose a present or potential hazard to human health and the environment when improperly transported, treated, stored, disposed of or otherwise managed and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- (1) The fractionation column bottoms or heavy end sludges contain 3% ethyl chloride\*, 22% dichloroethanes, 32% trichloroethylene, and 43% heavy chlorinated organics. 1,2-Dichloroethane is a suspected carcinogen and trichloroethylene and many of the heavy chlorinated organics in the wastes have been identified by the Agency as exhibiting substantial evidence of being carcinogenic.
- (2) The wastes traditionally have been managed by land disposal. Information obtained from telephone contacts with manufacturers\*\* indicates that some of the wastes are also incinerated in thermal destruction facilities. The substances in the wastes, if not managed properly, could be emitted to the air if the wastes are inadequately incinerated or improperly land disposed, or could leach from improperly managed or designed landfills and injection wells to reach humans and other environmental receptors. Hexachlorobenzene (a typical heavy chlorinated organic in column bottoms) has been shown to bioaccumulate in animal and human tissues through inhalation following mismanagement

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\*The Agency is aware that ethyl chloride is highly ignitable, with a flash point of -58°F. Generators are, of course, responsible for determining if these wastes are ignitable, even though listed for toxicity only.

\*\*Those manufacturers requested to remain anonymous.

during transportation and improper disposal. Trichloroethylene (another waste component) has shown to have leached into well water from waste disposal sites.

- (3) A large quantity (a combined total of about 35,000 metric tons per year) of these wastes are generated annually.

## II. INDUSTRY PROFILE

In 1979, there were reported to be six plants in the U.S. with capacity to produce about 330,000 metric tons/year of ethyl chloride.<sup>(1)</sup> Two of the plants are located in Texas, two in Louisiana, one in New Jersey and one in California. The average plant produces about 64,000 metric tons/year. The range for individual plants is about 35,000 to 100,000 metric tons/year. Since most of the ethyl chloride produced is used for the manufacturing of tetraethyl lead, production is on the decline.

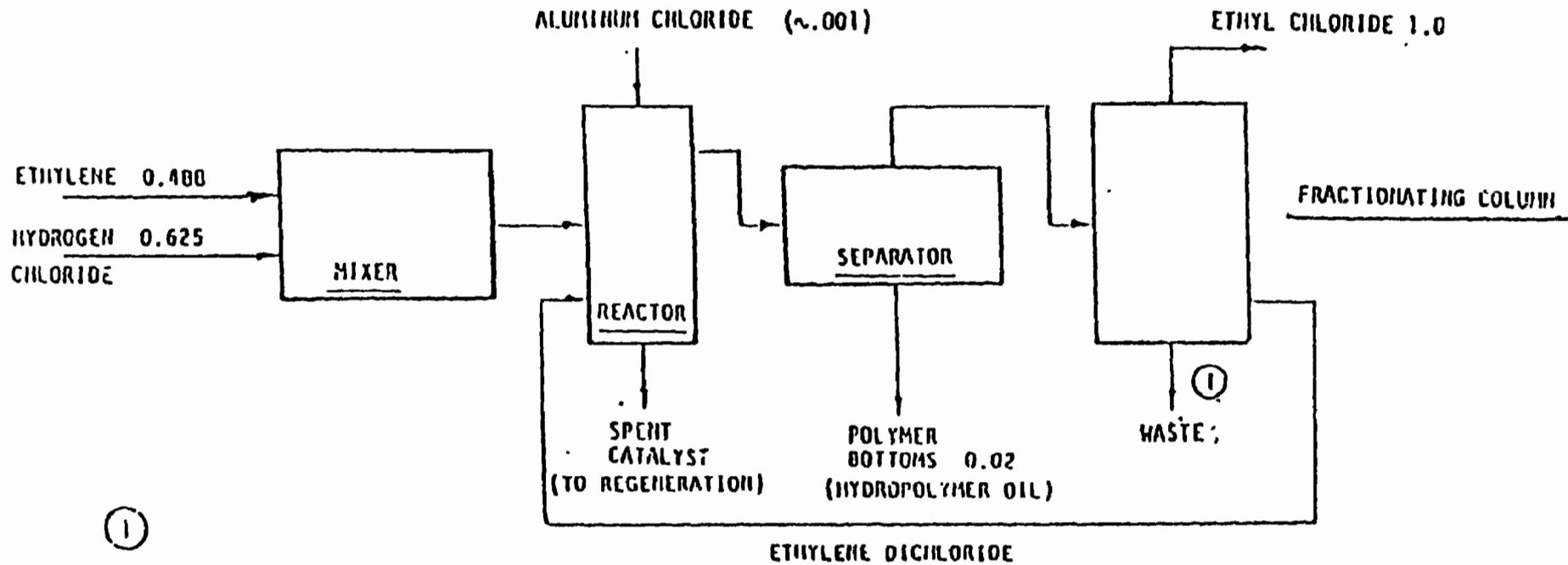
## III. MANUFACTURING PROCESS DESCRIPTION

Most of the ethyl chloride produced is manufactured by catalytic hydrochlorination of ethylene.<sup>(1)</sup> A process flow diagram is given in Figure 1. Ethylene and anhydrous hydrogen chloride gases are mixed and reacted at 35-40°C in the presence of an aluminum chloride catalyst. The reaction is exothermic. The vaporized products are fed into a column or "flash drum" where crude ethyl chloride is separated from heavier polymers. The polymer bottoms are a salable by-product. Finally, the crude ethyl chloride is refined by fractionation. The fractionation waste (on figure 1), or heavy ends, is composed of 3% ethyl chloride, 22% dichloroethanes, 32% trichloroethylene, and 43% heavy chlorinated organics.<sup>(2)</sup> This is the waste stream listed in this document.

## IV. WASTE GENERATION AND MANAGEMENT

The heavy ends from the fractionating column are generated at a rate

BASIS: 1 KG ETHYL CHLORIDE



①

WASTE FROM FRACTIONATING COLUMN-LIQUID

ETHYL CHLORIDE 0.003  
DICHLOROETHANES 0.02  
TRICHLOROETHYLENE 0.03  
HEAVY CHLORINATED ORGANICS 0.04

Source: Reference (2)

Figure 1 Ethyl Chloride Manufacture

of about .093 tons per ton of ethyl chloride produced.<sup>(2)</sup> The total quantity of waste produced is, therefore, approximately 35,000 metric tons per year (based on the 1979 production figures).

The wastes from ethyl chloride manufacture are usually combined for disposal with chlorinated hydrocarbon wastes of similar composition generated in the manufacture of chlorinated solvents (chloromethanes) at the same plant site. In 1973, it was reported that the combined wastes were sent to land disposal.<sup>(2)</sup> More recent information indicates that some wastes are being incinerated in thermal destruction facilities (see p. 1, above).

## VI. DISCUSSION OF BASIS FOR LISTING

### A. HAZARDS POSED BY THE WASTE

As indicated earlier, the heavy ends from fractionation in ethyl chloride production contain 22% dichloroethanes, 32% trichloroethylene, and 43% heavy chlorinated organics (such as hexachlorobutadiene, and hexachlorobenzene<sup>(2)</sup>) many of which have been identified by the Agency as substances which exhibit substantial evidence of carcinogenicity. Further, all of the chlorinated organic constituents in the waste demonstrate acute aquatic toxicity, generally showing increasing toxicity with increasing chlorination. Should these compounds reach environmental receptors, the potential for resulting adverse effects would be extremely high.

These waste constituents are capable of migration. The solubility in water of these chlorinated compounds is quite high: dichloroethane - 8700 ppm<sup>(4)</sup>, trichloroethylene - 1000 ppm<sup>(5)</sup>, and hexachlorobenzene - 500 ppm<sup>(4)</sup>. The high solubilities of these constituents indicate a

strong propensity to migrate from inadequate land disposal facilities. Thus, improperly constructed or managed landfills (for example, landfills located in areas with permeable soils, or with inadequate leachate control practices) could easily fail to impede leachate formation and migration.

Once released from the matrix of the waste, these constituents could migrate through the soil to ground and surface waters utilized as drinking water sources. A number of actual damage incidents documenting the leaching of constituents from waste sites and subsequent to groundwater contamination (see Damage Incidents pp. 6-8) have occurred. These damage incidents also confirm that many of these chlorinated compounds are environmentally persistent, since they obviously persist in the environment long enough to reach environmental receptors.

Another problem which could result from improper landfilling of these wastes is the potential for contaminants to volatilize into the surrounding atmosphere. Volatilized waste constituents, hexachlorobenzene in particular, have caused actual damage (see Damage Incidents, 1-3, pp. 6-7). 1,2-Dichloroethane (60 mm Hg at 20°C)<sup>(4)</sup> is also highly volatile, and therefore, could volatilize and thus present an air pollution problem if improperly managed (for example, if landfilled without adequate cover).

More recent information indicates that some wastes are being incinerated in thermal destruction facilities. Inadequate incineration conditions (temperature plus residence time) can result in incomplete combustion and air emission of the harmful chemical substances contained in the wastes as well as degradation products.

The large quantities (a combined total of about 35,000 metric tons per year) of this waste disposed of annually is another area of concern to the Agency. As previously indicated, there are substantial concentrations

of these toxic constituents (22% dichloroethanes, 32% trichloroethylene, 43% heavy chlorinated organics) in the waste stream. The large quantities of these contaminants pose the danger of polluting large areas of ground and surface waters. Contamination could also occur for long periods of time, since large amounts of pollutants are available for environmental loading. All of these considerations increase the possibility of exposure to the harmful constituents in the wastes.

#### B. DAMAGE INCIDENTS

The constituents found in the ethyl chloride fractionation column wastes have been implicated in a number of past damage incidents.

There have been three damage incidents caused by one of the substances present in the heavy ends, hexachlorobenzene<sup>(3)</sup>:

(1) In Louisiana, hexachlorobenzene (HCB), a toxic industrial by-product, was dumped in a rural landfill where it sublimated. Cattle absorbed HCB in their tissues and 20,000 animals were quarantined by the State Department of Agriculture (Lazar, 1975). This incident illustrates the ability of HCB to bioaccumulate.

(2) In Southern Louisiana, industrial wastes containing hexachlorobenzene (HCB), a relatively volatile material, were transported over a period of time to municipal landfills in uncovered trucks. High levels of HCB have since been reported in the blood plasma of individuals along the route of transport. In a sampling of 29 households along the truck route, the average plasma level of HCB was 3.6 ppb with a high of 23 ppb. The average plasmas level of HCB in a control group was 0.5 ppb with a high of 1.8 ppb (Farmer et al., 1976). This incident illustrates the ability of HCB to get into the blood stream from inhalation.

(3) Hexachlorobenzene wastes were disposed in landfill sites in southern Louisiana. Some of the waste was covered following disposal, and some was not. Soil and plant samples taken near the landfill area showed a decreasing HCB content as distance from the landfill increased. The HCB levels in the plasma of landfill workers was reported to range from 2 to 345 ppb; the average level in a control group was 0.5 ppb with a high of 1.8 ppb. A study of the land disposal of the hexachlorobenzene wastes indicated that uncovered wastes released 317 kilograms per hectare per year (kg/ha/yr). This incident further illustrates the ability of HCB to present a hazard due to improper landfill management and inhalation.

There have also been three damage incidents resulting from the mismanagement of trichloroethylene, another waste constituent.

(1) In one incident in Michigan, an automotive parts manufacturing plant routinely dumped spent degreasing solutions on the open ground at a rate of about 1000 gallons per year from 1968 to 1972. Trichloroethylene was one of the degreasing solvents present in the spent solutions. Beginning in 1973, trichloroethylene in nearby residential wells was detected at levels up to 20 mg/l. The dump site was the only apparent source of possible contamination (6). This illustrates the migratory potential and persistence of improperly disposed trichloroethylene.

(2) In a second incident, also in Michigan, an underground storage tank leaked trichloroethylene which was detected in local groundwater up to four miles away from the land(7). This also illustrates the migratory potential of trichloroethylene.

(3) In April of 1974, a private water well in Bay City, Michigan became contaminated by trichloroethylene. The only nearby source of this

chemical was the Thomas Company (which replaced the well with a new one). The company claimed that, although it had discharged trichloroethylene into the ground in the past, it had not done so since 1968. Nevertheless, in May, 1975, two more wells were reported to be contaminated with trichloroethylene at concentrations of 20 mg/l and 3 mg/l, respectively.(3) This further illustrates the migratory potential and persistence of this compound.

C. Health and Ecological Effects

1. 1,2-Dichloroethane

Health Effects - 1,2-Dichloroethane is a carcinogen.(9) In addition, this compound and several of its metabolites are highly mutagenic (10, 11). 1,2-Dichloroethane crosses the placental barrier and is embryotoxic and teratogenic (12 - 16), and has been shown to concentrate in the milk of nursing mothers.(17) Exposure to this compound can cause a variety of adverse health effects including damage of the liver, kidneys and other organs, internal hemorrhaging and blood clots (18). 1,2-Dichloroethane is a designated priority pollutant under Section 307(a) of the CWA. Additional information and specific references on adverse health effects of 1,2-dichloroethane can be found in Appendix A.

Ecological Effects - Values for a 96-hour static LC<sub>50</sub> for bluegills ranged from 236 to 300 mg/l.(19)

Regulations - OSHA has set the TWA at 50 ppm. DOT requires the containers for this chemical to carry a warning that it is a flammable liquid.

The Office of Air, Radiation and Noise has completed pre-regulatory assessment of 1,2-dichloroethane under Sections 111 and 112 of the Clean Air Act. Pre-regulatory assessments are also being conducted

by EPA's Office of Water and Waste Management under the Safe Drinking Water Act and by the Office of Toxic Substances under the Toxic Substances Control Act.

Industrial Recognition of Hazard - Sax, in Dangerous Properties of Industrial Materials, rates 1,2-dichloroethane as highly toxic upon ingestion and inhalation.

## 2. Trichloroethylene

Priority Pollutant - Trichloroethylene is listed as a priority pollutant in accordance with §307(a) of the Clean Water Act of 1977.(20)

Health Effects - Trichloroethylene is identified as a carcinogen.(39) It has also been identified by the Agency as a compound exhibiting substantial evidence of carcinogenicity. Trichloroethylene has been shown, both through acute and chronic exposure, to produce disturbances of the central nervous system and other neurological effects(22,23,24). Trichloroethylene has been found to cause hepatocellular carcinoma in mice. Additional information on the adverse effects of trichloroethylene can be found in Appendix A.

## 3. Hexachlorobenzene (HCB)

Priority Pollutant - HCB is listed as a priority pollutant under Section 307(a) of the Clean Water Act.

Health Effects - Hexachlorobenzene (HCB) has produced cancers in animal species(25,26) and has been recognized by the Agency to be carcinogenic.(39) Other animal studies have shown that HCB crosses the placental barrier to produce toxic effects and was lethal to fetuses.(27) Hexachlorobenzene is stored for long periods in body fat. Chronic exposure

to HCB has been shown to result in damage to the liver and spleen.(28)

It has also been demonstrated that at doses far below those which are lethal, HCB enhances the body's capability to toxify, rather than detoxify, other foreign organic compounds present in the body through its metabolism.(29)

The recommended ambient criterion(31) level for HCB in wastes is 1.25 nanograms per liter. Actual measurements, on the other hand, of finished drinking water in certain geographic areas have been measured at levels up to six times the recommended criterion designed to protect human health, demonstrating the mobility and persistence of the material.(38)

Ecological Effects - Hexachlorobenzene is very persistent.(32)

It has been reported to move through the soil into the groundwater.(21)

Movement of hexachlorobenzene within surface water systems is projected to be widespread.(30) Movement to this degree will likely result in

exposure to aquatic life forms in rivers, ponds, and reservoirs.

Similarly, potential exposure to humans is likely where water supplies are drawn from surface waters.

Hexachlorobenzene is likely to contaminate accumulated bottom sediments within surface water systems and bioaccumulate in fish and other aquatic organisms.(30)

Regulatory Regulation of Hazard - Ocean dumping of hexachlorobenzene is prohibited. An interim food contamination tolerance of 0.5 ppm has been established by FDA.

Additional information on the adverse effects of hexachlorobenzene can be found in Appendix A.

4. Hexachlorobutadiene(HCBD)

Priority Pollutant - Hexachlorobutadiene is considered a priority pollutant under Section 307(a) of the CWA.

Routes of Exposure - oral-very toxic

Health Effects - Hexachlorobutadiene (HCBD) has been found to be carcinogenic in animals.(23,39) Upon chronic exposure of animals by the DOW Chemical Company and others, the kidney appears to be the organ most sensitive to HCBD.(34,35,36,37)

The proposed human health criterion level for this compound in water is .77 ppb.

Ecological Effects - Movement of HCBD within surface water systems is projected to be widespread.(30)

HCBD is likely to contaminate accumulated bottom sediments within surface water systems and is likely to bioaccumulate in fish and other aquatic organisms.(30)

The USEPA (1979) has estimated that the BCF is 870 for the edible portion of fish and shellfish consumed by Americans.

Hexachlorobutadiene is persistent in the environment.(32) It has been reported to move through soil into groundwater.

Industrial Recognition of Hazard - Hexachlorobutadiene is considered to have a high toxic hazard rating via both oral and inhalation routes (Sax, Dangerous Properties of Industrial Material).

Additional information on the adverse effects of hexachlorobutadiene can be found in Appendix A.

## REFERENCES

1. Stanford Research Institute. 1979 Directory of chemical producers - U.S.A. SRI International. Menlo Park, CA. 1979.
2. U.S. EPA. Assessment of industrial hazardous waste practices: Organic chemicals, pesticides and explosive industries. EPA No. SW118c. NTIS PB No. 251 307. January, 1976.
3. U.S. EPA. Open files. Hazardous Site Control Branch, WH-548, U.S. EPA. 401 M St., S.W., Washington, D.C. 20460. Contact Hugh Kauffman. (202) 245-3051.
4. Dawson, English and Petty. Physical chemical properties of hazardous waste constituents. 1980.
5. Patty, F. A., ed. Industrial hygiene and toxicology. V.II. Interscience Publishers, New York. 1963.
6. Michigan Department of Natural Resources - Geological Survey Division. Case History #48.
7. Schellenbarger, P. New charge hits Air Force. The Detroit News. May 17, 1979.
8. Not used in text.
9. National Cancer Institute. Bioassay of 1,2-dichloroethane for possible carcinogenicity. U.S. Department of Health, Education and Welfare, Public Health Service, National Institutes of Health, National Cancer Institute, Carcinogenesis Testing Program. DHEW Publication No. (NIH) 78-1305. NTIS PB No. 285 968. January 10, 1978.
10. McCann, J., E. Choi, E. Yamasaki, and B. Ames. Detection of carcinogens as mutagenic in the Salmonella/microsome test: Assay of 300 chemicals. Proc. Nat. Acad. Sci. USA. 72(2):5135-5139. 1975.
11. McCann, J., V. Simmon, D. Streitwieser, and B. Ames. Mutagenicity of chloroacetaldehyde, a possible metabolic product of 1,2-dichloroethane (ethylene dichloride), chloroethanol (ethylene cholohydrin), vinyl chloride, and cyclophosphamide. Proc. Nat. Acad. Sci. 72 (8):3190-3193.
12. Vozovaya, M. Changes in the estrous cycle of white rats chronically exposed to the combined action of gasoline and dichloroethane vapors. Akush. Genacol. (kiev) 47(12):65-66. 1971.
13. Vozovaya, M. Development of offspring of two generations obtained from females subjected to the action of dichloroethane. Gig. Sanit. 7:25-28. 1974.

14. Vozovaya, M. The effect of low concentrations of gasoline, chloroethane and their combination on the generative function of animals and on the development of progeny. Gig. Tr. Prof. Zabo. 7:20-23. 1975.
15. Vozovaya, M. Effect of low concentrations of gasoline, dichloroethane and their combination on the reproduction function of animals. Gig. Sanit. 6:100-102. 1976.
16. Vozovaya, M.A. The effect of dichloroethane on the sexual cycle and embryogenesis of experimental animals. Akush. Genecol. (Moscow) 2:57-59. 1977.
17. Urusova, T.P. (About a possibility of dichloroethane absorption into milk of nursing women when contacted under industrial conditions.) Gig. Sanit. 18(3):36-37. 1953. (Rus.)
18. Parker, J.C., et al. Chloroethanes: A review of toxicity. Amer. Indus. Hyg. Assoc. J. 40:A 46-60. March, 1979.
19. U.S. EPA. Chlorinated ethanes: Ambient water quality criteria. NTIS PB No. 297 920. 1979.
20. U.S. EPA. State Regulations Files. Hazardous Waste State Programs, WH-565, U.S. EPA, 401 M St., S.W., Washington, D.C. 20460. Contact Sam Morekas. (202) 755-9145. January, 1980.
21. Not used in text.
22. Nomiyama, K., and H. Nomiyama. Metabolism of trichloroethylene in human sex differences in urinary excretion of trichloroacetic acid and trichloroethanol. Int. Arch. Arbeitsmed. 28:37. 1971.
23. Bardodej, A., and J. Vyskocil. The problem of trichloroethylene in occupational medicine. AMA Arch. Ind. Health 13:581. 1956.
24. McBirney, B.S. Trichloroethylene and dichloroethylene poisoning. AMA Arch. Ind. Hyg. 10:130. 1954.
25. Cabral, J. R. P., et al. Carcinogenic activity of hexachlorobenzene in hamsters. Nature (London) 269:510. 1977.
26. Cabral, J. R. P., et al. Carcinogenesis study in mice with hexachlorobenzene. Tox. Appl. Pharmacol. 45:323. 1978.
27. Grant, D. L., et al. Effect of hexachlorobenzene on reproduction in the rat. Arch. Environ. Contam. Toxic. 5:207. 1977.
28. Koss, G., et al. Studies on the toxicology of hexachlorobenzene. III. Observation in a long-term experiment. Arch. Toxicol. 40:285. 1978.

29. Carison, G. P. Induction of cytochrome P-450 by halogenated benzenes. Biochem. Pharmacol. 27:361. 1978.
30. U.S. EPA. Technical support document for aquatic fate and transport. U.S. EPA Environmental Research Lab. Athens, GA. 1980.
31. U.S. EPA. Chlorinated benzenes: Ambient water quality criteria. NTIS PB No. 297 919. 1979.
32. U.S. EPA. Water-related environmental fate of 129 priority pollutants. EPA No. 440/4-79-029b. 1979.
33. Kociba, R. J. Results of a two-year chronic toxicity study with hexachlorobutadiene in rats. Amer. Ind. Hyg. Assoc. 38:589. 1977.
34. Kociba, R.J., et. al. Toxicologic study of female rats administered hexachlorabutadiene or hexachlorobenzene for 30 days. Dow Chemical Company. 1971.
35. Schwetz, et al. Results of a reproduction study in rats fed diets containing hexachlorobutadiene. Toxicol. Appl. Pharmacol. 42:387. 1977.
36. Schroit, et. al. Kidney lesions under experimental hexachlorobutadiene poisoning. Aktual. Vpo. Gig. Epidemiol. 73. CA:81:73128F (translation). 1972.
37. Hobbs, F.D., and C.W. Stuewe. Emission control options for the synthetic organic chemicals manufacturing industry: Carbon tetra-chloride and perchloroethylene, (hydrocarbon chlorinolysis process), abbreviated product report. EPA Contract No. 68-02-2577. March, 1979.
38. U.S. EPA. Preliminary assessment of suspected carcinogens in drinking water. Report to Congress. U.S. EPA. Washington, D.C. EPA No. 560/4-75-003. 1975.
39. U.S. EPA. Office of Research and Development, Carcinogen Assessment Group List of Carcinogens. April 22, 1980.

Response to Comments - Heavy Ends or Distillation Residues from the  
Production of Ethyl Chloride

One commenter requested that the Agency reassess its interpretation of what materials actually constitute waste in the production of ethyl chloride. The commenter pointed out that many of these materials are not discarded and never become wastes; instead, they are further processed within a short time to other products and manufacturing intermediates.

In reviewing the available information, the Agency has evidence to indicate that these wastes traditionally have been managed by land disposal. Additionally, information obtained from telephone contacts with manufacturers of ethyl chloride indicates that some of these wastes are also incinerated in thermal destruction facilities. Therefore, these wastes are "discarded" and, thus, meet the definition of a solid waste (§261.2) and will continue to be listed as hazardous. However, this waste is not always discarded, as evidenced by the comments received (i.e., these wastes may be used, reused, recycled or reclaimed). As discussed in the preamble to the Part 261 regulations promulgated on May 19, 1980 (45 FR 33091 - 33095), the Agency has concluded that it does have jurisdiction under Subtitle C of RCRA to regulate waste materials that are used, reused, recycled or reclaimed. A large number of comments have been received, however, which challenge this conclusion. The Agency is giving these comments serious consideration, but has not presently finalized this portion of the regulations. Therefore, until a final decision is reached with respect to materials which are used, reused, recycled or reclaimed, the following guidance is offered to individual plants to assist them in determining their responsibilities under the hazardous waste regulations:

- o If the listed waste is always discarded at the individual plant, the waste always is subject to the full set of hazardous waste regulations.
- o If the listed waste is sometimes discarded at a particular plant, but sometimes used, reused, recycled or reclaimed, (not used as an intermediate) the waste would only be subject to the full set of hazardous waste regulations when discarded. When used, reused, recycled or reclaimed the waste would be subject to the special requirements for listed wastes contained in §261.6(b) of the hazardous waste regulations (45 FR 33120).
- o If the listed waste is typically processed through the next step of the process within a short time, the material does not meet the definition of a solid waste (i.e., is an intermediate product), and is therefore not subject to the hazardous waste regulations (45 FR 33119, and see discussion at 45 FR 33093-094).

## LISTING BACKGROUND DOCUMENT

## ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER PRODUCTION

Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production. (T)

Heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production. (T)

I. Summary of Basis for Listing:

The heavy ends from the distillation of ethylene dichloride in ethylene dichloride (EDC) production, and the distillation of vinyl chloride in production of vinyl chloride monomer (VCM) contain toxic chemicals and chemicals that are carcinogenic, mutagenic, or teratogenic. The waste constituents of concern are ethylene dichloride, trichloroethanes (1,1,1/1,1,2), tetrachloroethanes (1,1,1,2/1,1,1,2), vinyl chloride, vinylidene chloride, chloroform, and carbon tetrachloride.

The Administrator has determined that the heavy ends generated during the purification (distillation) of crude EDC and VCM is a solid waste stream which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of, or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. Of the compounds present in the ethylene dichloride and vinyl chloride monomer wastes, many are known or suspected carcinogens, and several are mutagenic and/or teratogenic.
2. Disposal of these wastes is accomplished partially by use of landfills, which, if improperly designed or operated, could result in leaching of hazardous substances into ground or surface water and subsequent risk of human exposure to the dangerous components of the waste.
3. Hydrocarbons, such as those predominating in this waste, are highly mobile and persistent in the soil profile and saturated subsurface, and have been responsible for many reported cases of ground water pollution. Enhancing this potential for ground and surface water pollution is the fact that most of this waste is produced and disposed of in Gulf coastal areas where water tables and rainfall are generally high.
4. The total combined waste generation for the balanced EDC/VCM process is estimated to be 170-370 million lb./yr. Such a large volume of waste containing dangerous constituents justifies imposition of strict controls.

## II. Source of the Wastes and Typical Disposal Practices

### A. Profile of the Industry (1,2)

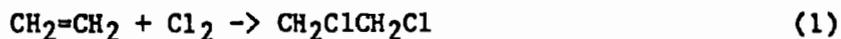
Ethylene dichloride (EDC) and vinyl chloride monomer (VCM) are produced at 20 plants within the United States. Table 1 presents a list of EDC and VCM producers. EDC is produced by both the direct chlorination of ethylene and the oxychlorination of ethylene. VCM is produced by the thermal cracking (dehydrochlorination) of EDC. The waste streams listed in this document thus arise in many cases out of a common production process. Figure 1 presents a summary of the chemical reactions involved in producing EDC and VCM.

Production in 1978 was 6.346 million metric tons for EDC and 3.776 million metric tons for VCM (Table 1).

TABLE 1. PRODUCERS AND 1978 PRODUCTION CAPACITIES OF  
ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER  
(metric tons/yr) (1, 2)

Company	Plant location	Ethylene dichloride	Vinyl chloride monomer
Allied	Baton Rouge, Louisiana	272,000	136,000
Borden	Geismar, Louisiana	-	136,000
Conoco	Lake Charles, Louisiana	544,000	318,000
Diamond Shamrock	Deer Park, Texas	145,000	-
	LaPorte, Texas	-	454,000
Dow	Freeport, Texas	726,000	91,000
	Oyster Creek, Texas	499,000	318,000
	Plaquemine, Louisiana	590,000	363,000
Ethyl	Baton Rouge, Louisiana	318,000	136,000
	Pasadena, Texas	113,000	-
Goodrich	Calvert City, Kentucky	454,000	454,000
PPG	Lake Charles, Louisiana	585,000	181,000
	Guayanilla, Puerto Rico	485,000	277,000
Monochem	Geismar, Louisiana	-	136,000
Shell	Deer Park, Texas	635,000	381,000
	Norco, Louisiana	544,000	318,000
Stauffer	Long Beach, California	141,000	77,000
Union Carbide	Taft, Louisiana	68,000	-
	Texas City, Texas	68,000	-
Vulcan	Geismar, Louisiana	159,000	-
	TOTALS	6,346,000	3,776,000

ETHYLENE DICHLORIDE VIA DIRECT CHLORINATION OF ETHYLENE



ETHYLENE DICHLORIDE VIA OXYCHLORINATION OF ETHYLENE



VINYL CHLORIDE MONOMER VIA THERMAL CRACKING OF ETHYLENE DICHLORIDE



ETHYLENE DICHLORIDE AND VINYL CHLORIDE MONOMER  
VIA THE BALANCED PROCESS

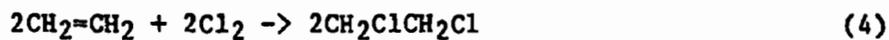


Figure 1. Alternative methods of producing ethylene dichloride and vinyl chloride monomer.

Manufacturing Process, Waste Composition and Waste Management (1, 65, 66)

As noted above, ethylene dichloride (EDC) is produced by two processes: the direct chlorination of ethylene and the oxychlorination of ethylene. Vinyl chloride monomer (VCM) is produced by the thermal cracking of EDC yielding hydrogen chloride (HCL) as a by-product. In the "balanced process", ethylene is converted to EDC in two equally sized production units utilizing direct chlorination and oxychlorination of ethylene. The HCl by-product produced by the thermal cracking of EDC to form VCM and by direct ethylene chlorination is used as feed for the oxychlorination unit. The flow diagram for the balanced process is given in Figure 2. For those VCM plants that purchase EDC, the by-product HCL is recovered and sold or used in other hydrochlorination processes.

1. EDC Production by Direct Chlorination of Ethylene

The chemical reaction for the direct chlorination of ethylene to produce ethylene dichloride is equation (1) in Figure 1. Ethylene is chlorinated catalytically in a vapor- or liquid-phase reaction, in the presence of ethylene dibromide to prevent polychlorination, at temperatures ranging between 50°C and 150°C and at 10 to 20 psig pressure. The catalysts used are metallic chlorides; e.g., ferric, aluminum, copper, or antimony. Commercially, ferric chloride is employed as a catalyst in the liquid-phase system. Yields are reported at approximately 90% based on ethylene.(3)

Chlorine is mixed with ethylene and fed to a reactor where the reaction takes place in the liquid phase with an excess of EDC. The reaction is exothermic (217.6 MJ/mole or 52 kcal/mole), and heat is removed by jacketed walls, internal cooling coils, or external heat

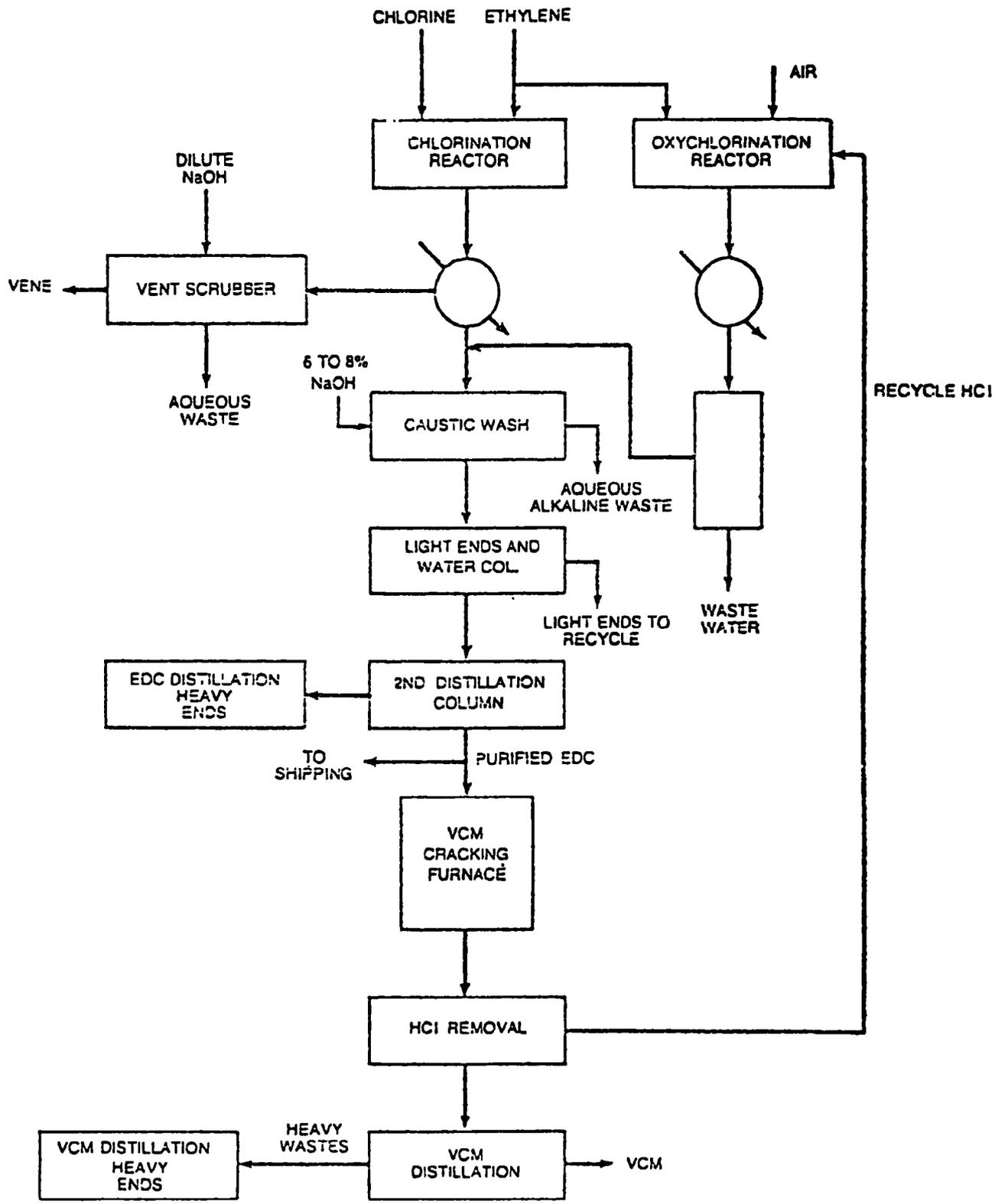


Figure 2. PRODUCTION OF EDC & VCM  
 Modified from references 1, 65, 66

exchange. A liquid and a vapor stream are obtained from the reactor.

The overhead vapor effluent from the reactor is condensed in a water-cooled or refrigerated heat exchanger to condense any ethylene dichloride present in the vapor stream. Noncondensables are sent through a scrubber fed with diluted sodium hydroxide to remove small amounts of hydrogen chloride and chlorine gas before venting to the atmosphere.

Liquid effluent from the reactor, consisting mainly of crude ethylene dichloride, is cooled, then washed with a 6% to 8% caustic solution. Water is removed either by coalescing and phase separation, or by phase separation and light ends distillation. Ethylene dichloride is obtained as overhead in a heavy ends distillation column. Based on common practice in the chlorinated hydrocarbon industry, these distillation bottoms, consisting of heavy ends, are sent to disposal or used as a feedstock in another process; this is the first waste stream of concern in this document.

A list of the pollutants found in the distillation column heavy ends in the direct chlorination process are presented in Table 2, along with their amounts.

Table 2. HEAVY ENDS FROM DIRECT CHLORINATION [1]

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Ethylene dichloride - 3.3 lb/ton of ethylene dichloride
1,1,2 Trichloroethane - 5.39 lb/ton of ethylene dichloride
Tetrachloroethane - 5.39 lb/ton of ethylend dichloride
Tars - trace

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## 2. EDC Production by Oxychlorination of Ethylene

The chemical reaction for the oxychlorination of ethylene to produce ethylene dichloride follows is presented as equation (2) in Figure 1.

Air and hydrogen chloride react with ethylene in a fluidized- or fixed-bed catalytic process to produce ethylene dichloride. The catalyst used is a mixture of copper chloride and other chlorides. Reactor temperature varies between 180°C and 280°C, and pressure ranges from 340 to 680 kPa gauge (50 to 100 psig). Yields are over 90% based on ethylene, depending on the presence of excess ethylene or hydrogen chloride. Excess hydrogen chloride favors the reaction.

Stoichiometric amounts of ethylene, anhydrous hydrogen chloride, and air are fed to a catalytic reactor. The air is compressed and preheated prior to entering the reactor as a means of initiating the reaction. Conversion of ethylene is virtually complete in one pass through the reactor. The reaction is highly exothermic, and heat is recovered as steam, with internal cooling, using coils or fixed-bed multitube reactors which resemble a heat exchanger, with the catalyst contained inside the tubes, while coolant flows through the shell.(3)

Effluent from the reactor is cooled by either direct water quench or indirect heat exchange. Condensed effluent is sent to a phase separator. Noncondensable gases consisting mainly of nitrogen are contacted in an absorber with either water or aromatic solvent for removal of HCl and recovery of ethylene dichloride before venting to the atmosphere. The organic liquid product obtained in the phase separator joins the stream of the product from direct chlorination and is contacted with aqueous

caustic soda to neutralize any remaining hydrogen chloride.

Effluent from the neutralizer is distilled for removal of light ends consisting of water and light chlorinated hydrocarbon impurities. The light ends are recovered as overhead and sent to waste disposal.\* Bottoms from the distillation column, which consist mainly (96% to 98%) of ethylene dichloride, are sent to the final products purification or distillation column. Pure ethylene dichloride is obtained as overhead and sent to storage. The heavy ends from the EDC purification (or distillation) column are the waste stream at issue here. Table 3 indicates pollutants contained in the EDC heavy ends from the oxychlorination process.

Table 3. HEAVY ENDS FROM OXYCHLORINATION [2]

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Ethylene dichloride - 4.6 lb/ton of ethylene dichloride
Trichloroethane - 4.6 lb/ton of ethylene dichloride
Heavy chlorinated compounds - 5.8 lb/ton of ethylene dichloride

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Disposal of these wastes is expected to be by incineration or landfilling, based on common practice in the chlorinated hydrocarbon industry or used as a feedstock in another process.

### 3. VCM Production

Vinyl chloride is produced from purified EDC. The purified EDC is thermally cracked to yield crude VCM and hydrochloric acid (HCl). The HCl is recovered and used as feed to the oxychlorination reactor.

\*/ This waste stream is not presently listed as hazardous.

Crude VCM is distilled to yield pure VCM. Heavy ends from VCM distillation are disposed of as waste or are recycled for additional thermal cracking and/or further chlorination to form other chlorinated organic products.

It should be noted that the balanced process generates both EDC heavy ends and VCM heavy ends. In an integrated plant some heavy ends from the VCM plant are cycled to the ethylene dichloride still. In a non-integrated plant, they are stripped of the ethylene dichloride, which is to be recycled to the VCM unit. In either case, the ultimate residue when wasted is expected to be disposed of by incineration or landfill, based on common practice in this industry (i.e., the chlorinated hydrocarbon industry).

The bottoms from the ethylene dichloride plant are partially cycled to a downstream chlorination unit where the residual heavy ends are partially retained and partially sent to ~~landfill~~. Based on common industry practice, disposal is expected to be by incineration or landfill.

The heavy ends waste discharge (for both EDC heavy ends and VCM heavy ends) for a plant producing ethylene dichloride and vinyl chloride monomer by the balanced process is estimated to consist principally of the components listed in Table 4 below:

Table 4 Estimated Heavy Ends Waste Discharge for EDC and VCM Production by the Balanced Process

Ethylene Dichloride	3-5 lb/ton of EDC
Trichloroethane	4-5 lb/ton of EDC
Tetrachloroethane	2-5 lb/ton of EDC
Heavy Chlorinated Compounds (Tars)	3-6 lb/ton of EDC

This estimate assumes that the major constituents of EDC heavy ends and VCM heavy ends will be the same - a reasonable supposition since not all the carbon bonds in the EDC feedstock will be cracked by dehydrochlorination, so that these waste constituents will remain to be separated as heavy ends in the VCM distillation step.

The quantities shown in Table 4 are averages derived from the heavy end composition data shown in Tables 2 and 3. Relative concentrations of major waste constituents may be determined from the amounts of constituents shown in Tables 2-4.

In addition to the major components listed in Table 4, the combined ethylene dichloride - vinyl chloride monomer heavy ends waste discharge also is expected to contain lesser quantities of the following compounds:

- Vinyl Chloride
- Vinylidene Chloride
- Trichloroethylene
- Tetrachloroethylene
- Chloroform
- Carbon Tetrachloride

The postulated reaction pathways for these constituents (briefly stated) are as follows. Vinyl chloride is likely to be present since it is the product and would not be removed completely in the distillation step. Vinylidene chloride would result from the dehydrochlorination of trichloroethylene (a major constituent of EDC heavy ends) trichloroethylene would result from the dehydrochlorination of tetrachloroethane (another major

constituent of EDC heavy ends). Trichloroethylene could in turn be chlorinated to form tetrachloroethylene. Chloroform could result from the dehydrochlorination of feedstock EDC, and could in turn be chlorinated to form carbon tetrachloride.

### III. Discussion of Basis for Listing

#### A. Hazards Posed by the Waste

##### 1. Quantities of Wastes Generated

Based on annual production capacities of approximately 14 billion pounds (6.35 million metric tons) for ethylene dichloride intermediate and 8.3 billion pounds (3.78 metric tons) for vinyl chloride monomer end product, as much as 30 million pounds of ethylene dichloride and 30 million pounds each of trichloroethane and tetrachloroethane may be present in the heavy ends waste generated from the production of these substances each year. Very large quantities of other waste constituents will also be generated. Thus, extremely large quantities of waste constituents are available for environmental release. Additionally, ethylene dichloride, 1,1,2-trichloroethane, and 1,1,2,2-tetrachloroethane--also present in high concentrations--are known carcinogens, while 1,1,1-trichloroethane and 1,1,1,2-tetrachloroethane, also present in high concentrations, are suspected carcinogens. In addition, the waste also contains lesser quantities of vinyl chloride, vinylidene chloride, tetrachloroethylene, trichloroethylene, and chloroform, all of which are known carcinogens. A number of the compounds found in this waste also exhibit mutagenic or tetraogenic effects, including 1,1,1-trichloroethane, 1,1,2-trichloroethane, and the tetrachloroethanes. Should release occur, large-scale contamination of the environment is likely. Moreover, contamination will be prolonged,

since large amounts of the pollutants are available for environmental loading. Attenuative capacity of individual disposal sites also could be exhausted due to the large quantities of pollutants available. These considerations themselves justify hazardous waste listing status.

Further, as shown below, the waste constituents are capable of migration, mobility, and persistence if improperly managed. Indeed, numerous damage incidents involving these waste constituents have actually occurred.

## 2. Exposure Pathways of Concern

Based on common industry practice, current methods for disposal of this waste are by incineration or landfilling. Improper management of either method can result in substantial hazard. Improper incineration could result in serious air pollution through release of toxic fumes. This may occur when incineration facilities are operated in such a way that combustion is incomplete (i.e., inadequate conditions of temperature, mixing and residence time) resulting in airborne dispersion of hazardous vapors containing partially combusted organics, newly formed organic compounds, and hydrogen chloride. Phosgene is an example of a partially chlorinated organic which is produced by the decomposition or combustion of chlorinated organics by heat.<sup>(61, 62)</sup> Phosgene has been used as a chemical warfare agent, and is extremely toxic. Improper incineration thus could present a significant opportunity for exposure of humans, wildlife and vegetation in the vicinity of these operations to risk through direct contact.

Improper disposal in landfills can also lead to substantial environmental hazard. Migration to and subsequent contamination of ground

and surface waters is a particular danger. All of the waste constituents of concern tend to be highly soluble in water (with the exception of vinyl chloride, which is a gas), with solubilities ranging from 800 mg/l (carbon tetrachloride) to 8700 mg/l (ethylene dichloride (Appendix B)). Thus, these waste constituents will tend to migrate in high concentrations under even relatively mild environmental conditions. Improperly sited landfills (for example, in areas with highly permeable soils, or in areas where soil is low in attenuative capacity) or improperly managed (for instance, landfills with inadequate leachate collection or monitoring systems) could easily prove inadequate to prevent waste migration.

Once these waste constituents migrate from the waste, they are likely to persist in groundwater for long periods of time (App. B). Thus, improperly designed landfills could well lead to human and environmental exposure, and attendant substantial hazard in light of the hazardous nature of the waste constituents.

An air inhalation pathway is an additional exposure route of concern. Of the waste constituents, ethylene dichloride, the trichloroethanes, the tetrachloroethanes, chloroform, and carbon tetrachloride all tend to be relatively to highly volatile, with vapor pressures ranging from 5mm Hg. (tetrachloroethanes) to 116 mm Hg. (chloroform) (App. B.). Vinyl chloride is already a gas, so it also poses a substantial air pollution hazard. Inadequate site cover could therefore lead to escape of volatile waste constituents and resulting contamination of air in the vicinity surrounding the site.

There is, therefore, a strong potential that landfilling of these wastes will ultimately result in pollution of nearby groundwater

by ethylene dichloride, the trichloroethanes, the tetrachloroethanes, and other similar waste components. This is enhanced by the fact that most of this waste is produced and, presumably, disposed of in Gulf coast areas (see Table 1) where water tables are generally shallow and rainfall is relatively high.

There is also the possibility that components of this waste could enter surface waters, either by mishandling of the waste prior to disposal or by migration of individual compounds through groundwater to points of discharge to surface waters.

In surface waters, the chlorinated ethanes and ethylenes will tend to volatilize due to their high vapor pressures. However, traces will probably remain for extended periods of time. Chloroform, one of the waste components, in fact, has been shown to persist almost indefinitely in surface water. (App. B)

### 3. Actual Damage Incidents

Actual damage incidents confirm these waste constituents' ability to migrate and persist and cause substantial hazard if improperly managed. The chlorinated ethanes and ethylenes--such as those which predominate in this waste--are the classes of organic pollutants being identified far more often than any other pollutant types in current groundwater pollution incidents. For example, ethylene dichloride, (1,2-dichloroethane) has been found in groundwater from public water supply wells at Bedford, Massachusetts, where the source is believed to be industrial operations upstream.(4)

At the Llangollen landfill in Delaware, dichloroethane (ethylene

dichloride and/or 1,1-dichloroethane) has been found migrating from the landfill through nearby ground water.(5) In New Jersey, seepage from landfilled wastes near the CPS chemical company resulted in contamination of nearby ground water by trichloroethane and tetrachloroethane.(6) 1,1,1-Trichloroethane was detected in ground water at Acton, Massachusetts, where the source is believed to be a settling lagoon at a nearby manufacturing plant.(4) Extensive contamination of ground water by trichloroethylene has also been reported in southeast Pennsylvania.(7) Trichloroethylene has also been found in school and basement air, and in residential basements in Love Canal.(64)

Field reports such as these clearly indicate that the release of low molecular weight chlorinated hydrocarbons into the soil will result in pollution of groundwater with the potential risk of substantial adverse health effects. This is further substantiated by recent laboratory studies in which 1,1,2-trichloroethane, chloroform, and similar compounds were observed to move through a four foot profile of sandy soil with little retardation relative to water and no apparent degradation.(8) Also, field studies in the Netherlands and California have shown that low molecular weight chlorinated hydrocarbons, such as those occurring in this waste, are highly mobile and persistent in the saturated ground water environment.(9, 10)

In light of the highly dangerous character of the constituents of concern in the waste, some of which are likely to be present in high concentrations, the Agency would require strong assurance that these constituents will not migrate and persist if improperly landfilled or incinerated. Data in fact indicate that these constituents may well migrate and persist via a number of exposure pathways. Thus, these

wastes clearly should be listed as hazardous.

B. Health and Ecological Effects

1. Ethylene Dichloride

Health Effects - Ethylene dichloride (1,2-dichloroethane)

has been shown to cause cancer in laboratory animals.(11) Ethylene dichloride is extremely toxic (oral rat LD<sub>50</sub> = 12 mg/Kg). In addition, this compound and several of its metabolites are highly mutagenic.(12) 1,2-Dichloroethane crosses the placental barrier and is embryotoxic and teratogenic.(13-17) It has also been shown to concentrate in milk.(18) Exposure to this compound can cause a variety of adverse health effects including damage to the liver, kidneys and other organs. It can also cause internal hemorrhaging and blood clots.(19) Ethylene dichloride (1,2-dichloroethane) is designated as a priority pollutant under section 307(a) of the CWA. Additional information and specific references on adverse effects of ethylene dichloride can be found in Appendix A.

Ecological Effects - Values for a 96 hour static LC<sub>50</sub> for bluegills range from 256 to 300 mg/l.(20)

Regulatory Recognition of Hazard - OSHA has set the TWA at 50 ppm. DOT requires the containers for this chemical to carry a warning that it is a flammable liquid. The Office of Air Pollution and Noise has completed the preregulatory assessment of 1,2-dichloroethane under sections 111 and 112 of the Clear Air Act. Preregulatory assessments are also being conducted by EPA's Office of Water and Waste Management under the Safe Drinking Water Act and by the Office of Toxic Substances under the Toxic Substances Control Act. Ethylene dichloride is currently being studied by the Consumer Product Safety Commission under the Consumer Product Safety Act.

Industrial Recognition of Hazard - Sax in Dangerous Properties of Industrial Materials rates 1,2-dichloroethane as highly toxic upon ingestion and inhalation.

2. 1,1,1-Trichloroethane (Methyl Chloroform)\*

Health Effects - The area of greatest health concern regarding 1,1,1-trichloroethane exposure involves its potential for mutagenic, teratogenic and carcinogenic effects. In vitro studies have indicated that 1,1,1-trichloroethane is slightly mutagenic with or without activation.(20,57,58) These studies were performed using the Ames system which is characteristically insensitive to chlorinated hydrocarbons. 1,1,1-Trichloroethane was also positive in an in vitro mammalian cell transformation assay.(19) However, the results of two animal carcinogen bioassay studies were inconclusive due to design and experimental problems.(18,20,56) The NCI is currently re-evaluating the carcinogenic potential of 1,1,1-trichloroethane. Studies of the teratogenic potential of 1,1,1-trichloroethane are also suggestive; however, more studies are needed to make a conclusive statement.(56)

Other than psychophysiological effects, 1,1,1-trichloroethane exposure at or below the OSHA-PEL (350 ppm) does not result in either acute or chronic toxic complications. At very high concentrations (710,000 ppm), however, 1,1,1-trichloroethane produces cardiovascular and CNS narcotic effects, and can cause death from cardiac failure. Animal studies as well as accidental human exposure, have shown that,

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\*The discussion on the health and environmental effects of 1,1,1-trichloroethane has been modified as a result of comments received on the hazard-ousness of 1,1,1-trichloroethane on other listings.

at these high inhalation concentrations, 1,1,1-trichloroethane produces a "chlorinated hydrocarbon" type of microscopic pathology liver and kidneys (fatty infiltration, cellular necrosis) which is characterized as being much less severe than that produced by carbon tetrachloride or trichlorethylene. Additional information and specific references on the adersion effects of 1,1,1-trichlorethane can be found in Appendix A.

Ecological Effects - Lethal concentrations (LC<sub>50</sub>, 96 hour values) are reported ranging from 33 mg/l (Dab), and 70 mg/l (Sheepshead minnow) to 69.7 mg/l (Bluegill) and 105 mg/l (Flathead minnow). (24,56)

1,1,1-Trichloroethane in common with other volatile hydrocarbons, volatilizes from water to an appreciable extent. However, retransport to water from the atmosphere and decreased volatilization rates from stagnant water render the aquatic compartment an important sink for 1,1,1-trichloroethane. The major ecological concern, however, is its possible role as an ozone depleter. In recent years there has been considerable concern over human activities appreciably altering the levels of ozone in the stratosphere. The tropospheric lifetime of 1,1,1-trichloroethane is believed to be in the range of 4-12 years, and it has been estimated that 10-20 percent of the 1,1,1-trichloroethane molecules released at the earth's surface will eventually reach the stratosphere. (59) Studies simulating conditions obtained at high altitudes have shown (60) that the lax resident time of 1,1,1-trichloroethane in the stratosphere and the high solar uv intensity will result in its eventual total destruction yielding free Cl atoms which are known to destroy stratospheric ozone.

Regulations - 1,1,1-Trichloroethane is designated as a priority pollutant under Section 307(a) of the CWA. OSHA has set the TWA at 350 ppm. EPA has recommended an ambient water quality criterion at 15.7 mg/l. Because of wide use and exposure, and the inadequacy of currently available information, the TSCA Interagency Testing Committee has recommended (55) further evaluation to establish the carcinogenicity, mutagenicity and teratogenicity and other chronic effects of 1,1,1-trichloroethane.

Industrial Recognition of Hazard - Sax Dangerous Properties of Industrial Materials lists 1,1,1-trichloroethane as carcinogenic and moderately toxic.

### 3. 1,1,2-Trichloroethane

Health Effects - 1,1,2-Trichloroethane has been shown to cause cancer in mice.(27) It has also been identified by the Agency as a compound exhibiting substantial evidence of carcinogenicity. (67) There is evidence that 1,1,2-trichloroethane is mutagenic and may be embryo toxic or cause teratogenic effects.(13-17,28-30) 1,1,2-Trichloroethane is considered toxic [oral rat LD<sub>50</sub> = 1140 mg/Kg].

Like the other compounds of this type, the trichloroethanes are narcotics, produce central nervous system effects, and can damage the liver, kidney and other organs.(19) 1,1,2-Trichloroethane is designated as a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of 1,1,2-trichloroethane can be found in Appendix A.

Ecological Effects - Aquatic toxicity data are limited with only three acute studies in freshwater fish and invertebrates with

doses ranging from 10,700 to 22,000 mg/l.(20)

Regulations - OSHA has set the TWA at 10 ppm (skin).

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, lists 1,1,2-trichloroethane as being moderately toxic by inhalation, ingestion and skin absorption.

#### 4. Tetrachloroethanes

Health Effects - 1,1,2,2-Tetrachloroethane has been shown to produce liver cancer in laboratory mice.(31) It has also been identified by the Agency as a compound exhibiting substantial evidence of being carcinogenic. (67) It is also shown to be very toxic [oral rat LD<sub>50</sub> = 200 mg/Kg]. In addition, passage of 1,1,1,2-tetrachloroethane across the placental barrier has been reported.(29) In Ames Salmonella bioassay 1,1,2,2-tetrachloroethane was shown to be mutagenic.(32) Occupational exposure of workers to 1,1,2,2-tetrachloroethane produced neurological damage, liver and kidney ailments, edema, and fatty degeneration of the heart muscle.(33) Both 1,1,1,2-tetrachloroethane and 1,1,2,2-tetrachloroethane are designated as priority pollutants under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of the tetrachloroethanes can be found in Appendix A.

Ecological Effects - Freshwater invertebrates are sensitive to 1,1,2,2-tetrachloroethane with a lethal concentration of 7-8 mg/l being reported.(20) USEPA estimates the BCF to be 18.

Regulations - OSHA has set the TWA at 5 ppm (skin) for 1,1,2,2-tetrachloroethane.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, lists 1,1,2,2-tetrachloroethane as

being highly toxic via ingestion, inhalation and skin absorption.

#### 5. Trichloroethylene

Health Effects - Trichloroethylene has been demonstrated to induce liver cancer in mice.(34) It has also been identified by the Agency as a compound exhibiting substantial evidence of carcinogenicity.(67) This compound may be absorbed into the body by inhalation, by ingestion, or by absorption through the skin.(34)

An excess of lung, cervical, and skin cancers and a slight excess of leukemias and liver cancers were observed in a study of 330 deceased laundry and dry-cleaning workers who had been exposed to carbon tetrachloride, trichloroethylene, and tetrachloroethylene.(35)

Trichloroethylene is mutagenic in bacteria and yeast and in spot tests for somatic mutations in mice.(36)

Numerous fatalities resulting from anesthesia with trichloroethylene and from industrial intoxications have been reported.(34) Acute and chronic inhalation of trichloroethylene effects the central nervous system. Toxic effects on the liver and other organs can occur from exposure by any route, and there is an indication that the hepatotoxic effect of trichloroethylene is enhanced by concomitant exposure to ethanol or isopropyl alcohol.(34,36) Additional information and specific references on the adverse effects of trichloroethylene can be found in Appendix A.

Ecological Effects - Freshwater fish (bluegill) are poisoned by trichloroethylene during a 96 hour exposure to 40-60 mg/l concentration range.(37)

Regulations - OSHA has set a TWA at 100 ppm.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, lists trichloroethylene as a high systemic toxicant via inhalation and moderate via ingestion.

#### 6. Tetrachloroethylene

Health Effects - Tetrachloroethylene is a carcinogen in laboratory mice.(38) It has also been identified by the Agency as a compound exhibiting substantial evidence of carcinogenicity.(67) The compound can be absorbed into the body via inhalation, by ingestion, and through the skin to increase its toxic effects.(30)

It has also been reported to be mutagenic and to cause transformation of mammalian cells.(30) An excess of lung, cervical and skin cancers and a slight excess of leukemias and liver cancers were observed in a study of 330 deceased laundry and dry-cleaning workers who had been exposed to carbon tetrachloride, trichloroethylene, and tetrachloroethylene.(35)

There is some evidence that tetrachloroethylene may be teratogenic. Repeated exposures to tetrachloroethylene vapors produced a variety of pathological change in the liver ranging from fatty degeneration to neurosis in rats, rabbits and guinea pigs. Exposure to this compound may also effect the kidneys and other organs. It also causes central nervous system effects and gastrointestinal symptoms.(30)

A case of "obstructive jaundice" in a six week old infant has been attributed to tetrachloroethylene in breast milk.(40) Additional information and specific references on the adverse effects of tetrachloroethylene can be found in Appendix A.

#### 7. Vinyl Chloride (VCM)

Health Effects - Vinyl Chloride has been shown to be

a carcinogen in laboratory studies.(41,42) It has also been identified by the Agency as a compound exhibiting substantial evidence of carcinogenicity.(67) This finding has subsequently been supported by epidemiological findings.(43,44) Vinyl chloride is very toxic [oral rat LD<sub>50</sub> = 500 mg/Kg]. Acute exposure to vinyl chloride results in anaesthetic effects as well as uncoordinated muscular activities of the extremities, cardiac arrhythmias(45) and sensitization of the myocardium.(46) In severe poisoning, the lungs are congested and liver and kidney damage occur.(47) A decrease in white blood cells and an increase in red blood cells was also observed and a decrease in blood clotting ability.(48) Vinyl chloride is designated as a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of vinyl chloride can be found in Appendix A.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, lists vinyl chloride as having a moderate toxic hazard rating via inhalation.

#### 8. Vinylidene Chloride

Health Effects - Vinylidene chloride has been shown to cause cancer in laboratory animals.(49,50) It has also been identified by the Agency as a compound exhibiting substantial evidence of carcinogenicity.(67) It is very toxic [oral rat LD<sub>50</sub> = 200 mg/Kg](49). Chronic exposure to vinylidene chloride can cause damage to the liver and other vital organs as well as causing central nervous system effects. Additional information and specific references on the adverse effects of vinylidene chloride can be found in Appendix A.

Regulations - OSHA has set the TWA at 10 ppm.

Industrial Recognition of Hazard - DOT requires containers to be labeled "flammable liquid".

The toxic hazard of vinylidene chloride is suspected of being similar to vinyl chloride which is moderately toxic via inhalation, Sax, Dangerous Properties of Industrial Materials.

#### 9. Chloroform

Health Effects - Chloroform has been shown to be carcinogenic in animals and is recognized as a suspect human carcinogen.(51) It has also been identified by the Agency as a compound exhibiting substantial evidence of carcinogenicity(67). Tangential evidence links human cancer epidemiology with chloroform contamination of drinking water.(52,53) Chloroform has also been shown to induce fetal toxicity and skeletal malformation in rat embryos.(54,55) Chronic exposure causes liver and kidney damage and neurological disorders.(52) Additional information and specific references on the adverse effects of chloroform can be found in Appendix A.

Ecological Effects - USEPA has estimated that chloroform accumulates fourteenfold in the edible portion of fish and shellfish.(52) The USEPA has recommended that contamination by chloroform not exceed 500 mg/l in freshwater and 620 mg/l in marine environment.(52)

Regulations - OSHA has set the TWA at 2 ppm. FDA prohibits use of chloroform in drugs, cosmetics, and food contact materials. The Office of Water and Waste Management has proposed regulation of chloroform under Clean Water Act 311 and is in the process of developing regulations under Clean Water Act 304(a). The Office of Air, Radiation, and Noise is conducting preregulatory assessment of chloroform under the Clean Air Act. The Office of Toxic Substances has requested additional

testing of chloroform under Section 4 and is conducting a preregulatory assessment under the Federal Insecticide, Fungicide and Rodenticide Act.

Industrial Recognition of Hazard - Chloroform has been given a moderate toxic hazard rating for oral and inhalation exposures, Sax, Dangerous Properties of Industrial Materials.

10. Carbon Tetrachloride

Health Effects - Carbon tetrachloride is estimated to occur in this waste stream in low concentrations, but is a very potent carcinogen.(56) It has been identified by the Agency as a compound exhibiting substantial evidence of carcinogenicity.(67) The toxic effects [oral rat LD<sub>50</sub> = 2800 mg/Kg] of carbon tetrachloride are amplified by both the habitual and occasional ingestion of alcohol.(57)

Obese individuals are especially sensitive to the toxic effects of carbon tetrachloride because the compound accumulates in body fat.(58) It also causes harmful effects in humans as the undernourished, those suffering from pulmonary diseases, gastric ulcers, liver and kidney diseases, diabetes, or glandular disturbances.(59)

The recommended criterion level in water designed to protect humans from the toxic effects of carbon tetrachloride is 2.6 mg/l.(57) In measurements made during the National Organics Monitoring Survey of 113 public water systems sampled, 11 of these systems had carbon tetrachloride at levels at or exceeding the recommended safe limit.(60) Carbon tetrachloride is a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse

effects of carbon tetrachloride can be found in Appendix A.

Ecological Effects - Movement of carbon tetrachloride within surface water systems is projected to be widespread. (See App. B) Movement to this degree will likely result in exposure to aquatic life forms in rivers, ponds and reservoirs.

Carbon tetrachloride is likely to be released to the atmosphere from surface water systems. In the atmosphere, carbon tetrachloride is slowly decomposed to phosgene, a highly toxic gas. In the incineration of carbon tetrachloride-containing wastes, phosgene is likely to be emitted under incomplete combustion conditions.

Regulations - OSHA has set a TWA for carbon tetrachloride at 10 ppm. Carbon tetrachloride has been banned by the Consumer Product Safety Commission under the Hazardous Substances Act.

Industrial Recognition of Hazard - According to Sax, Dangerous Properties of Industrial Materials, the oral toxicity rating is high.

#### IV. References

1. U.S. EPA. Industrial process profiles for environmental use: Chapter 6, The industrial organic chemicals industry. EPA No. 600/2-77-023f. February, 1977.
2. U.S. EPA. Engineering and cost study of air pollution control for petrochemical industry-V.3. Ethylene dichloride manufacture by oxychlorination. EPA No. 450/3-73-006-c. November 1974.
3. U.S. EPA. Source assessment: Chlorinated hydrocarbons manufacture. EPA No. 600/2-79-019g. August, 1979.
4. Water quality issues in Massachusetts. Chemical contamination, special legislative commission on water supply. September, 1979.
5. DeWalle, F.P., and E.S.K. Chian. Detection of trace organics in well water near a solid waste landfill. In Proceedings; 34th Industrial Waste Conference, Lafayette. May 8-10, 1979. Purdue University. Ann Arbor Science, 1980. pp. 742-752.
6. Memo from Roy Albert to E.C. Beck, Administrator EPA Region II, Drinking Water Contamination of New Jersey Well Water. March 31, 1978.
7. Buller, R.D. Trichloroethylene contamination of ground water case history and mitigative technology. Presented at American Geophysical Union Fall Meeting, December 3-7, San Francisco, CA. 1979.
8. Wilson, J.T., and C.G. Enfield. Transport of organic pollutants through unsaturated soil. Presented at American Geophysical Union Fall Meeting, December 3-7, San Francisco, CA. 1979.
9. Zoeteman, B.C.J. Persistent organic pollutants in river water and ground water of the Netherlands. In Proceedings; Third International Symposium on Aquatic Pollutants. October 15-17. Jekyll Island, Ga. 1979.
10. Roberts, P.V., P.L. McCarty, Mr. Reinhard, and J. Schriener. Organic contaminant behavior during ground water recharge. In Proceedings; The 51st Annual Conference of the Water Pollution Control Federation. October 1-6. Anaheim, CA. 1978.
11. National Cancer Institute. Bioassay of 1,2-dichloroethane for possible carcinogenicity. U.S. Department of Health, Education and Welfare, Public Health Service, National Institutes of Health, National Cancer Institute, DHEW Publication No. (NIH) 78-827. 1978. NTIS PB No. 285 968. 1978.

IV. References (Continued)

- 12a. McCann, J., E. Choi, E. Yamasaki, and B. Ames. Detection of carcinogens as mutagenic in the Salmonella/microsome test: Assay of 300 chemicals. Proc. Nat. Acad. Sci. USA 72(2): 5135-5139, 1975a.
- 12b. McCann, J., V. Simmon, L. Streitwieser, and B. Ames. Mutagenicity of chloroacetaldehyde, a possible metabolic product of 1,2-dichloroethane (ethylene dichloride), chloroethanol (ethylene chlorohydrin), vinyl chloride, and cyclophosphamide. Proc. Nat. Acad. Sci. 72(8): 3190-3193. 1975.
13. Vozovaya, M. Changes in the estrous cycle of white rats chronically exposed to the combined action of gasoline and dichloroethane vapors. Akush. Geneko. (Kiev) 47(12): 65-66. 1971.
14. Vozovaya, M. Development of offspring of two generations obtained from females subjected to the action of dichloroethane. Gig. Sanit. 7:25-28. 1974.
15. Vozovaya, M. The effect of low concentrations of gasoline, dichloroethane and their combination on the generative function of animals. Gig. Sanit. 6:100-102. 1976.
16. Vozovaya, M. Effect of low concentrations of gasoline, dichloroethane and their combination on the reproductive function of animals. Gig. Sanit. 6:100-102. 1976.
17. Vozovaya, M.A. The effect of dichloroethane on the sexual cycle and embryogenesis of experimental animals. Akusk. Ginekol. (Moscow) 2:57-59. 1977.
18. Urusova, T.P. (About a possibility of dichloroethane absorption into milk of nursing women when contacted under industrial conditions.) Gig. Sanit. 18(3):36-37. 1953. (Rus)
19. Parker, J.C., et al. Chloroethanes: A review of toxicity. Amer. Ind. Hyg. Assoc. J., 40:46-60. March, 1979.
20. U.S. EPA. Chlorinated ethanes: Ambient water quality criteria (Draft). NTIS PB No. 297 920. 1979.
21. NCI. Bioassay of 1,1,1-trichloroethane for possible carcinogenicity. Carcinog. Tech. Rep. Ser. NCI-CG-TR-3. NTIS PB No. 265 082.
22. Price, P.J., et al. Transforming activities of trichloroethylene and proposed industrial alternatives. In Vitro 14:290. 1978.
23. U.S. EPA. In vitro microbiological mutagenicity of 81 compounds. In Vitro 14:290. 1980.

IV. References (Continued)

24. Schwetz, B.A., et al. Embryo- and feto-toxicity of inhaled carbon tetrachloride, 1,1-dichloroethane and methyl ethyl ketone in rats. Toxicol. Appl. Pharmacol. 28:452. 1974.
25. Walter, P., et al. Chlorinated hydrocarbon toxicity (1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene): A monograph. NTIS PB No. 257 185. 1976.
26. U.S. EPA. In-depth studies on health and environment impact of selected water pollutants. Contract No. 68-01-4646. 1979.
27. National Cancer Institute. Bioassay of 1,1,2-trichloroethane for possible carcinogenicity. U.S. Department of Health, Education, and Welfare, Public Health Service, National Institutes of Health, National Cancer Institute, DHEW Publication No. (NIH) 78-1324. NTIS PB No. 283 337. 1978.
28. Elovaara, E., et al. Effects of CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl<sub>3</sub>, TCE, PERC and Toluene in the development of chick embryos. Toxicology 12: 111-119. 1979.
29. Truhaut, R., N.P. Lich, H. Dutertre-Catella, G. Molas, V.N. Huyen. Toxicological study of 1,1,1,2-tetrachloroethane. Archives des Maladies Professionnelles, de Medicine du Travail et de Securite 35(6):593608. 1974.
30. Parker, J.C., et al. Health assessment document for 1,2-dichloroethane (ethylene dichloride). Review draft report. EPA Environmental Criteria and Assessment Office, Research Triangle Park. November, 1979.
31. National Cancer Institute. Bioassay of 1,1,2,2-tetrachloroethane for possible carcinogenicity. U.S. Department of Health, Education, and Welfare, Public Health Service, National Institutes of Health, National Cancer Institute, DHEW Publication No. (NIH) 78-827. NTIS PB No. 277 453. 1978.
32. Brem H., et al. The mutagenicity and DNA-modifying effect of haloalkanes. Cancer. Res. 34:2576. 1974.
33. National Institute for Occupational Safety and Health. Criteria for a recommended standard...occupational exposure to 1,1,2,2-tetrachloroethane. U.S. DHEW, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-121. NTIS PB No. 273 802. December, 1976.

IV. References(Continued)

34. Page, Norbert P., and J. L. Arthur. Trichloroethylene. Special occupational hazard review with control recommendations. DHEW Publication No. (NIOSH) 78-130. January, 1978.
35. Blair, et al. Causes of death among laundry and dry cleaning workers. Am. J. Publ. Health 69:508-511. 1979.
36. IARC Monographs. Evaluation of carcinogenic risk of chemicals to man. Trichloroethylene. Interagency for Research on Cancer. Lyon, France. World Health Organization. Vol. 20:545. 1979
37. U.S. EPA. Trichloroethylene: Ambient water quality criteria. NTIS PB No. 292 443. 1979.
38. National Cancer Institute. Bioassay of tetrachloroethylene for possible carcinogenicity. CAS No. 127-18-4, NCI-CG-TR-13, DHEW PB No. (NIH) 77-813. NTIS PB No. 272 940. 1977.
39. Not used in text.
40. Bignell, P.C., and H.A. Ellenberger. Obstructive jaundice due to a chlorinated hydrocarbon in breast milk. Con. Med. Assoc. J., 117:1047-1048.
41. Viola, P.L., et al. Oncogenic response of cat skin, lungs, and liver to vinyl chloride. Cancer Res. 31:516. 1971.
42. Maltoni, C., and G. Lefemine. Carcinogenicity bioassays of vinyl chloride. Am. N.Y. Acad. Sci. 246:195. 1975.
43. Creech and Johnson. Angiosarcoma of the liver in the manufacture of polyvinyl chloride. J. Occup. Med. 161:150. 1974.
44. Tabershaw, I.R., and Gaffey, W.R. Mortality study of workers in the manufacture of vinyl chloride and its polymers. J. Occup. Med. 16:509. 1974.
45. Oster, R.H., et al. Anesthesia XXVII narcosis with vinyl chloride. Anesthesiology 8:359. 1947.
46. Cair, J., et al. Anesthesia XXIV. Chemical constitution of hydrocarbons and cardiac automaticity. J. Pharmaceut. 97:1. 1949.
47. Torkerson, T.R., et al. The toxicology of vinyl chloride by repeated experience of laboratory animals. Amer. Ind. Hyg. Assoc. J. 22:304. 1961.
48. Lester D., et al. Effects of single and repeated exposures of humans and rats to vinyl chloride. Amer. Ind. Hyg. Assoc. J. 24:265. 1963.

IV. References (Continued)

49. Environmental Health Perspectives, 1977. Vol. 21, pp. 333.
50. U.S. EPA. Vinylidene chloride hazard profile. USEPA/ECAO Cincinnati, Ohio 45268. 1979.
51. National Cancer Institute. Report on carcinogenesis bioassay of chloroform. NTIS PB No. 264 018. 1976.
52. U.S. EPA. Trichloromethane (chloroform) hazard profile. USEPA/ECAO Cincinnati, Ohio 45268. 1979.
53. McCabe, L.J. Association between trihalomethanes in drinking water (NORS data) and mortality. Draft report. 1979.
54. Thompson, D.J., et al. Teratology studies on orally administered chloroform in the rat and rabbit. Toxicol. Appl. Pharmacol. 29:348. 1974.
55. Schwetz, B.A., et al. Embryo and fetotoxicity of inhaled chloroform in rats. Toxicol. Appl. Pharmacol. 28:442. 1974.
56. IARC monographs on the evaluation of carcinogenic risk of chemicals to man, V's. 1, 20. World Health Organization. 1972.
57. U.S. EPA. Carbon tetrachloride: Ambient water quality criteria document. NTIS PB No. 292 424. 1979.
58. U.S. EPA. Water-related environmental fate of 129 priority pollutants. EPA No. 440/4-79-029b. 1979.
59. Von Oettingen, W.F. The halogenated hydrocarbons of industrial and toxicological importance. In: Elsevier Monographs on Toxic Agents. E. Browning, Ed. 1964.
60. U.S. EPA. The national organic monitoring survey. Technical Support Division, Office of Water Supply, Washington, D.C. 20460. 1978
61. Edwards, J.B. Combustion formation and emission of trace species. Ann Arbor Science 1977.
62. NIOSH. Criteria for recommended standard: Occupational exposure to phosgene. HEW, PHS, CDC, NIOSH. NTIS PB No. 267 514. 1976.
63. Not used in text.

IV. References (Continued)

64. "Love Canal Public Health Bomb." A Special Report to the Governor and Legislature, New York State Dept. of Health. 1978.
65. Lowenheim and Moran. Faith, Keyes, and Clark's Industrial Chemicals. 4th ed., John Wiley and Sons, Inc. 1975.
66. Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed. John Wiley and Sons, Inc. 1979
67. U.S. EPA. Cancer Assessment Group, Office of Research and Development. List of carcinogens. April 22, 1980.

Response to Comments - Heavy Ends from the Distillation of Ethylene Dichloride in Ethylene Dichloride Production and Heavy Ends from the Distillation of Vinyl Chloride in Vinyl Chloride Monomer Production

One commenter raised several questions with respect to wastes K019 and K020 (Heavy ends from the distillation of ethylene dichloride in ethylene dichloride production and heavy ends from the distillation of vinyl chloride in vinyl chloride monomer production).

1. The commenter first requested that the Agency reassess its interpretation of what materials actually constitute waste in the production of ethylene dichloride and vinyl chloride monomer. The commenter pointed out that many of these materials are not discarded and never become wastes; instead they are further processed within a short time to other products and manufacturing intermediates.

In reviewing the available information, the Agency has evidence that these wastes traditionally have been managed by incineration or landfilling. Therefore, these wastes are "discarded" and, thus, meet the definition of a solid waste (§261.2) and will continue to be listed as hazardous. However, this waste is not always discarded, as evidenced by the comments received (i.e., these wastes may be used, reused, recycled or reclaimed). As discussed in the preamble to the Part 261 regulations promulgated on May 19, 1980 (45 FR 33091-33095), the Agency has concluded that it does have jurisdiction under Subtitle C of RCRA to regulate waste materials that are used, reused, recycled or reclaimed. A large number of

comments have been received, however, which challenge this conclusion. The Agency is giving these comments serious consideration but has not presently finalized this portion of the regulations. Therefore, until a final decision is reached with respect to materials which are used, reused, recycled or reclaimed, the following guidance is offered to individual plants to assist them in determining their responsibilities under the hazardous waste regulations:

- ° If the listed waste is always discarded at the individual plant, the waste always is subject to the full set of hazardous waste regulations.
- ° If the listed waste is sometimes discarded at a particular plant, but sometimes used, reused, recycled or reclaimed (not used as an intermediate), the waste would only be subject to the full set of hazardous waste regulations when discarded. When used, reused, recycled or reclaimed the waste would be subject to the special requirements for listed wastes contained in §261.6(b) of the hazardous waste regulations (45 FR 33120).
- ° If the listed waste is typically processed through the next step of the process within a short time, the material does not meet the definition of a solid waste (i.e., is an intermediate product), and is therefore not subject to the hazardous waste regulations (45 FR 33119, and see discussion at 45 FR 33093-094).

2. The commenter then questioned the Agency's assessment of the toxicity of chloroform and objects to the inclusion of chloroform

as a constituent of concern in this particular listing. Also, the commenter believes that EPA has no perspective of the significance of the aquatic toxicity data.

The Agency strongly disagrees with the commenter. Chloroform has been designated carcinogenic by the Cancer Assessment Group (CAG) after much detailed study of the literature, including the National Cancer Institute bioassay test results (see reference material on CAG assessment for more details). Additionally, chloroform has been shown to induce fetal toxicity and skeletal malformation in rat embryos. Although research regarding other types of toxicity are still being conducted, the Agency believes that there is sufficient justification so as not to remove chloroform as a basis for listing wastes K019 and K020.

The comment regarding EPA's lack of perspective on aquatic toxicity data is unclear and lacks supporting data, thus, no further comment will be made.

## LISTING BACKGROUND DOCUMENT

## FLUOROCARBON PRODUCTION

Aqueous spent antimony catalyst waste from fluoromethanes production. (T)

I. Summary of Basis for Listing

The production of chlorofluoromethanes via the liquid phase fluorination process results in the generation of an aqueous spent antimony catalyst waste which contains both toxic organic and inorganic substances, two of which are carcinogenic. The waste constituents of concern are antimony compounds, chloroform and/or carbon tetrachloride.

The Administrator has determined that the wastewater from the production of chlorofluoromethanes via the liquid phase fluorination process is a solid waste which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- (1) The waste stream contains significant quantities of antimony compounds, chloroform and/or carbon tetrachloride.\*

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\*Depending on the type of fluorocarbon being produced, either chloroform or carbon tetrachloride will be used as a raw material and appear in the waste stream as an excess reactant (see discussion, "Industry Profile and Process Description," below).

- (2) Chloroform, carbon tetrachloride, and antimony compounds are highly toxic. Chloroform and carbon tetrachloride has been evaluated by EPA as substances exhibiting substantial evidence of carcinogenicity. Carbon tetrachloride has been shown to be teratogenic.
- (3) Chloroform and carbon tetrachloride are resistant to water treatment methods and are therefore likely to appear in drinking water if allowed to migrate from the waste into drinking water sources. These two constituents are also volatile and may pose a threat to human health via an air exposure pathway if not properly managed. Antimony compounds will persist in the environment (in some form) virtually indefinitely; therefore, if allowed to migrate from the waste may contaminate drinking water sources for long periods of time.
- (4) It is estimated that approximately 30,000 to 60,000 lbs. of spent catalyst is generated annually by the two plants using liquid phase fluorination and will be in the aqueous waste stream. The substantial quantity of waste generated increases the possibility of exposure should mismanagement occur.
- (5) Damage incidents involving the contamination of groundwater by antimony compounds, chloroform and carbon tetrachloride confirm the ability of these waste constituents to be mobile, persistent, and cause substantial harm.\*

## II. Industry Profile and Process Description (29,30)

Chlorofluoromethanes are manufactured by the fluorination of chlorocarbons. Two different fluorination processes may be used: liquid phase or vapor phase. This document is concerned solely with the aqueous spent catalyst waste from the manufacture of the

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\*Although no data on the corrosivity of spent antimony catalyst is currently available, the Agency believes that this waste stream may have a pH greater than 12.5 and may therefore be corrosive. Under §§261.22 and 262.11, generators of this waste stream are responsible for testing their wastes in order to determine whether their waste is corrosive.

chlorofluoromethanes that are produced via liquid phase fluorination.\* The commercial products produced by this segment of the fluorocarbon industry include chlorotrifluoromethane (CClF<sub>3</sub>), dichlorodifluoromethane (CCl<sub>2</sub>F<sub>2</sub>), trichlorofluoromethane (CCl<sub>3</sub>F), and chlorodifluoromethane (CHClF<sub>2</sub>). Of the five (5) companies that manufacture these products, it is believed that two have plants that use the liquid phase fluorination process and generate the waste stream of concern:

	<u>Company</u>	<u>Location</u>	<u>Plant Size - Million Pounds Per Year</u>
(1)	DuPont	Antioch, CA Deepwater, NJ East Chicago, IN ** Louisville, KY Matague, MI	500
(2)	Allied Chemical	Baton Rouge, LA Danville, IL Elizabeth, NJ El Segundo, CA	190
(3)	Kaiser Aluminum & Chemical	Gramercey, LA	80
(4)	Pennwalt	Calvert City, KY Throughfare, NJ	60
(5)	Racon, Inc.	** Wichita, KS	50

Total: 880

(Source: reference 31)

\*In the vapor phase fluorination process, a proprietary, largely insoluble, metallic catalyst is used in place of the antimony catalyst. The vapor phase catalyst will tend to last longer and have lower concentrations of the constituents of concern than the antimony catalyst used in liquid phase fluorination.

\*\*These two plants use liquid phase fluorination and generate spent antimony chloride catalyst waste.

The chlorofluoromethanes in the product family of concern are manufactured by fluorinating either carbon tetrachloride (CCl<sub>4</sub>) or chloroform (CHCl<sub>3</sub>) using hydrogen fluoride (HF) and antimony pentachloride (SbCl<sub>5</sub>) as a catalyst (see Figure 1). Carbon tetrachloride is used as a starting material when trichlorofluoromethane (CCl<sub>3</sub>F), dichlorodifluoromethane (CCl<sub>2</sub>F<sub>2</sub>), and chlorotrifluoromethane (CClF<sub>3</sub>) are the desired products. (Tetrafluoromethane (CF<sub>4</sub>) is also formed as a co-product waste.) Chloroform is used as feedstock when chlorodifluoromethane (CHClF<sub>2</sub>) and dichlorofluoromethane (CHCl<sub>2</sub>F) are the desired products. (A small amount of trichlorotrifluoroethane (C<sub>2</sub>Cl<sub>3</sub>F<sub>3</sub>) and trifluoromethane (CHF<sub>3</sub>) are formed as co-product wastes.) In both processes, the chlorine (Cl) in the starting materials is successively replaced with fluorine (F). For example, starting with carbon tetrachloride (CCl<sub>4</sub>), and hydrogen fluoride, the reaction is carried out continuously to produce the product mix desired, usually a 50/50 blend of trichlorofluoromethane (CCl<sub>3</sub>F) and dichlorodifluoromethane (CCl<sub>2</sub>F<sub>2</sub>) as illustrated by the following equations:



The main features of the process are shown in Figure 1. During the process, the antimony pentachloride catalyst (SbCl<sub>5</sub>) is reduced to antimony trichloride (SbCl<sub>3</sub>). A slip



stream is taken from (F) (see Figure 1.) to remove an aliquot portion of the spent catalyst. After washing, the aqueous spent catalyst wastes (G) are sent to pits (H) where they are either disposed of or stored until further treatment. (The bulk of the antimony trichloride is recovered by the catalyst filter and dried and reactivated by chlorination to form antimony pentachloride, which is recycled to the fluorinator.)

### III. Waste Composition, Generation and Management

Based on knowledge of process chemistry and best engineering judgment, the spent catalyst wastewater from liquid phase fluorination is expected to contain significant concentrations of the following constituents:

(1) Spent antimony chloride catalyst not recovered by the catalyst filter. This spent catalyst wastewater will contain antimony trichloride as a metallic ion and other antimony compounds.

(2) Organic residues from feedstock materials. These will include either carbon tetrachloride or chloroform, depending on which fluorocarbons are being produced.

Based on an estimated production of 100 million lb/yr (at the Dupont, Louisville, and Racon plants), it is estimated

that 30-60 thousand lbs. of spent catalyst are generated annually and will be contained in the spent catalyst wastewater.\* The wastewater will also contain dissolved chloroform and carbon tetrachloride in maximum concentrations of about 0.8 gms/100 gms of wastewater (based on these constituents water solubilities). Undissolved chloroform and carbon tetrachloride will also be entrained in the wastewater unless the organic layer of the aqueous wastestream has been separated prior to disposal. These wastes are typically discharged to clay-lined pits (26) either for disposal or storage until further treatment.

#### IV. Discussion of Basis for Listing

##### A. Hazards Posed by Waste

As noted above, the waste components of concern are antimony compounds, carbon tetrachloride and/or chloroform. Antimony compounds, chloroform and carbon tetrachloride are highly toxic. Chloroform is a suspected carcinogen. Carbon tetrachloride is a very potent carcinogen and has also been shown to be teratogenic.

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\*This estimate is also based on data in "Fluorocarbon Hydrogen Fluoride Industry", EPA-600/2-77-023 February 1977. This quantity is believed significant, since large quantities of hazardous waste constituents are available for environmental release, increasing the risk of exposure should mismanagement occur.

### B. Exposure pathways and migratory potential

The waste constituents of concern may migrate from improperly designed or managed disposal or storage sites and contaminate ground and surface waters. Antimony trichloride is extremely soluble (601.6 gm/100 gm H<sub>2</sub>O @ 0°C), chloroform is highly soluble (2200 mg/l @ 25°C), and carbon tetrachloride is quite soluble (800 mg/l @ 20°C). Chloroform and carbon tetrachloride are also highly volatile: 160 mm Hg @ 20°C and 91 mm Hg @ 20°C, respectively (water has a volatility of about 17.5 mm Hg @ 20°C). (28)

Storage or disposal in clay-lined pits is the most usual management method for these wastes. This practice may be adequate to prevent soil and/or groundwater contamination if pits are properly constructed and managed. However, if these pits are not properly constructed, they can develop cracks or leaks through thin points in the wall with subsequent release of the waste into the environment, in light of the waste constituents' migratory potential. In any case, wastes are hazardous under RCRA even if they are properly managed in fact. The potential of the waste to cause substantial harm is the key factor, and these wastes are believed to have ample potential to cause substantial hazard.

These wastes also may cause harm via additional exposure pathways. There is also a danger of migration into or contamination of surface waters if the pits are improperly designed or managed. Thus inadequate flood control measures could result in washout or overflow of the wastes. If the wastes

are allowed to reach too high a level in the pits, the pits may overflow during periods of heavy rain, releasing their contents which may find their way into and contaminate surface water.

There is also a danger of migration into the atmosphere if the disposal sites are inadequately designed or managed. Since chloroform and carbon tetrachloride are highly volatile, they may escape into the air and present a hazard to human health via an air inhalation pathway. Thus, these hazardous constituents could migrate from disposal sites with inadequate cover.

Actual damage incidents confirm that these waste constituents are mobile, persistent and cause substantial hazard if improperly managed. The migratory potential of antimony compounds is confirmed by the fact that groundwater contamination from disposed antimony sludges has been observed in an Iowa incident (2).

The migratory potential via an air pathway of chloroform and carbon tetrachloride is confirmed by the fact that both constituents have been identified as air contaminants in both schools and basements of homes located at Love Canal, New York ("Love Canal Public Health Bomb", A Special Report to the Governor and Legislature, New York State Department of Health, 1978). Chloroform has also migrated from the

Love Canal site into surrounding basement sumps, demonstrating ability to migrate through soils. (Id.) Other incidents of groundwater contamination due to improper storage and burial of chloroform-containing wastes further confirm chloroform's ability to migrate through soils and contaminate groundwater. In one incident, chloroform was detected in a well at Dartmouth, MA. In a similar incident at Woburn, MA., chloroform migrated from an underground burial site to contaminate a municipal well in the vicinity (4).

Antimony, since it is an elemental metal, will persist indefinitely in some form in the environment. Antimony trichloride also reacts vigorously with moisture, generating heat and highly irritating hydrogen chloride gas. The antimony component which results from this reaction can also cause systemic effects (27).

The carbon tetrachloride and chloroform in the waste are volatile and if stored in an open clay pit will tend to slowly evaporate. Should the chloroform or carbon tetrachloride reach ground or surface water prior to evaporation, as both have been known to do (see above and p. 12), they could travel significant distances due to their resistance to microbial degradation (3). In addition, carbon tetrachloride and chloroform are resistant to water treatment and, if they are present in drinking water sources, are likely to appear in drinking water. (19,18) The incidents of the migration of these harmful constituents previously mentioned (see p. 9) demonstrate

that they may persist long enough to reach and cause harm to a receptor, via either a water (ground or surface) or air pathway.

C. Health and Ecological Effects

1. Chloroform

Health Effects - Chloroform has been recognized and regulated as a suspected carcinogen (32). It is also considered toxic [oral rat LD<sub>50</sub>=800 mg/kg] and has been evaluated by CAG as having substantial evidence of carcinogenicity. Tangential evidence links human cancer epidemiology with chloroform contamination (6) of drinking water. In laboratory studies, chloroform induces liver cancers in mice and causes kidney tumors in experimental rats (7). Chloroform was shown to induce fetal toxicity and skeletal malformation in rat embryos (8,9). Chloroform is a priority pollutant under Section 307(a) fo the CWA. Additionally information on the adverse health effexts of chloroform can be found in Appendix A.

Ecological Effects - The U.S. EPA has determined that chloroform accumulates fourteen-fold in the edible portion of fish and shellfish (10).

Regualtions - OSHA has set the time weighted average at 50 ppm.

Industrial Recognition of Hazard - Chlorofrom has been given a toxic hazard rating via oral routes by Sax in Dangerous Properties of Industrial Materials.

## 2. Carbon Tetrachloride

Health Effects - Carbon tetrachloride is a very potent carcinogen (11) and has also been shown to be teratogenic in rats when inhaled at low concentrations (12). It has also been evaluated by CAG as having substantial evidence of carcinogenicity. Chronic effects of this chemical on the human central nervous system have occurred following inhalation of extremely low concentrations (20 ppm), with death at 1000 ppm (13). Adverse effects of carbon tetrachloride on liver and kidney function (acute and often irreversible hepatic failure), and on respiratory and gastrointestinal tracts (14,15) have also been reported. The toxic effects of carbon tetrachloride are amplified by both the habitual and occasional ingestion of alcohol (16). Especially sensitive to the toxic effects of carbon tetrachloride are obese individuals because the compound accumulates in body fat (17). It also causes harmful effects in undernourished humans, those suffering from pulmonary diseases, gastric ulcers, liver or kidney diseases, diabetes, or glandular disturbances (18). Carbon tetrachloride is a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of carbon tetrachloride can be found in Appendix A.

Ecological Effects - In measurements made during the National Organics Monitoring Survey of 113 public water systems sampled, 11 of these systems had carbon tetrachloride at levels at or exceeding the recommended safe limit (19).

13. Association of American Pesticide Control Officials, Inc. Pesticide chemical official compendium. 1966 ed. p. 198. 1966.
14. Texas Medical Association. Texas Medicine 69:86. 1973.
15. Davis, Paul A. Carbon tetrachloride as an industrial hazard. JAMA 103:963-966. Jul.-Dec. 1934.
16. U.S. EPA. Carbon tetrachloride: Ambient water quality criteria document. NTIS PB No. 292 424. 1979.
17. U.S. EPA. Water-related environmental fate of 129 priority pollutants. EPA No. 440/4-79-0296. 1979.
18. Von Oettingen, W.F. The halogenated hydrocarbons of industrial and toxicological importance. In: Elsevier monographs on toxic agents. E. Browning, ed. 1964.
19. U.S. EPA. The National Organic Monitoring Survey. Technical Support Division, Office of Water Supply. U.S. EPA. Washington, D.C. 20460. 1978.
20. Brieger, H., et al. Industrial antimony poisoning. Ind. Med. Surg. 23:521. 1954.
21. Belyaeva, A.P. The effect of antimony on reproduction. Gig. Truda. Prof. Zabel. 11:32. 1967.
22. Gross, H. Toxicological study of calcium halophosphate phosphorus and antimony trioxide in acute and chronic toxicity and some pharmacological aspects. Arch. Ind. Health 11:473. 1955.
23. Schroeder, H.A. A sensible look at air pollution by metals. Arch. Environ. Health 21:798. 1970.
24. Schroeder, H.A., and L.A. Kraemer. Cardiovascular mortality, municipal water, and corrosion. Arch. Environ. Health 28:303. 1974.
25. Not used in text.
26. Personal Communication from Richard Deutsch of E.I. Dupont de Nemours and Company, Louisville, KY, December 1979.
27. Sax, N.I. Dangerous properties of industrial materials. 4th ed. Litton Education Publishing, Inc. 1975.

28. Dawson, English, and Petty. Physical chemical properties of hazardous waste constituents. 1980.
29. Kirk-Othmer. Encyclopedia of chemical technology. V.5. John Wiley and Sons, Inc., New York. 1964.
30. Lowenheim, F.A. and M.K. Moran. Faith, Keyes and Clark's industrial chemistry, 4th ed. John Wiley and Sons, Inc., New York. 1975.
31. Stanford Research Institute. Directory of chemical producers-United States. SRI International, Menlo Park, CA. 1979.
32. U.S. EPA. Office of Research and Development, Carcinogen Assessment Group. List of Carcinogens. April 22, 1980.

Response to Comments - Aqueous Spent Catalyst Waste from  
Fluoromethanes Production

Aqueous spent catalyst waste from fluoromethanes production (K021) is listed as hazardous because it contains a number of toxic constituents, including chloroform. One commenter objected to the inclusion of chloroform as a constituent of concern in this particular listing. Also, the commenter believes that EPA has no perspective of the significance of the aquatic toxicity data.

The Agency strongly disagrees with the commenter. Chloroform has been designated carcinogenic by the Cancer Assessment Group (CAG) after much detailed study of the literature, including the National Cancer Institute bioassay test results (see reference material on CAG assessment for more details). Additionally, chloroform has been shown to induce fetal toxicity and skeletal malformation in rat embryos. Although research regarding other types of toxicity are still being conducted, the Agency believes that there is sufficient justification to continue to include chloroform as a basis for listing waste K021.

The comment regarding EPA's lack of perspective on aquatic toxicity data is unclear and lacks supporting data, thus, no further comment will be made.

## LISTING BACKGROUND DOCUMENT

### PHENOL/ACETONE PRODUCTION

- ° Distillation Bottom Tars from the Production of Phenol/  
Acetone from Cumene. (T)\*

#### I. Summary of Basis for Listing

Distillation bottom tars from the production of phenol/acetone from cumene contains toxic and potentially carcinogenic organic substances. These include phenol and polycyclic aromatic hydrocarbons (PAH) as the pollutants of concern.

The Administrator has determined that the solid waste from phenol/acetone production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA.

This conclusion is based on the following considerations:

1. Approximately 100-220 million pounds of these wastes containing phenol and polycyclic aromatic hydrocarbons from tars are generated per year at 11 plants in the United States.
2. Tars containing polycyclic aromatic hydrocarbons are demonstrated carcinogens and mutagens, as well as being toxic. Phenol is toxic.
3. There is potential for mismanagement of the waste by leakage during transport or storage, by improper disposal allowing leaching, or by incomplete incineration or combustion.

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\*The Agency believes that the listing description "distillation bottom tars" is more accurate than the originally proposed description "heavy tars". The stream listed in this document does not, however, differ from the one initially proposed.

4. The waste tars persist in the environment, and phenol can spread rapidly in ground or surface water, posing a risk of exposure to these hazardous compounds to humans.

## II. Sources of Waste and Typical Disposal Practices

### A. Profile of the Industry

Phenol/acetone is produced from cumene in eleven manufacturing plants scattered throughout nine states. Production data from 1978 have been reported to be 1,915 MM\* lb phenol and 1,171 MM lb acetone<sup>(1)</sup>.

### B. Manufacturing Process<sup>(13,14)</sup>

There are two steps in the manufacturing process: (1) oxidation of cumene to cumene hydroperoxide, and (2) cleavage of the hydroperoxide to form phenol and acetone. (A process flow chart is contained as Figure I below.) Cumene hydroperoxide is the first main reaction product when cumene is oxidized with air at 130°C in an aqueous sodium carbonate medium. The reaction mix is circulated to a vacuum column where unreacted cumene is separated from the mix and a cumene hydroperoxide concentration of about 80% is obtained in the bottoms product. Recovered cumene is recycled to the reactor. Any alpha methyl styrene contained in the recovered cumene is separated by distillation and sold or incinerated. However, not all of the alpha methyl styrene may be separated at this point. The 80% cumene hydroperoxide cumene mixture is then reacted with 10-25% sulfuric acid at 60°C and co-mixed with an inert solvent (such as benzene) to extract organic material from the aqueous acid. The mixture is allowed to settle. The acid phase is separated out and recycled to the process. The organic layer remaining is neutralized with dilute sodium hydroxide. The

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\*MM - one million

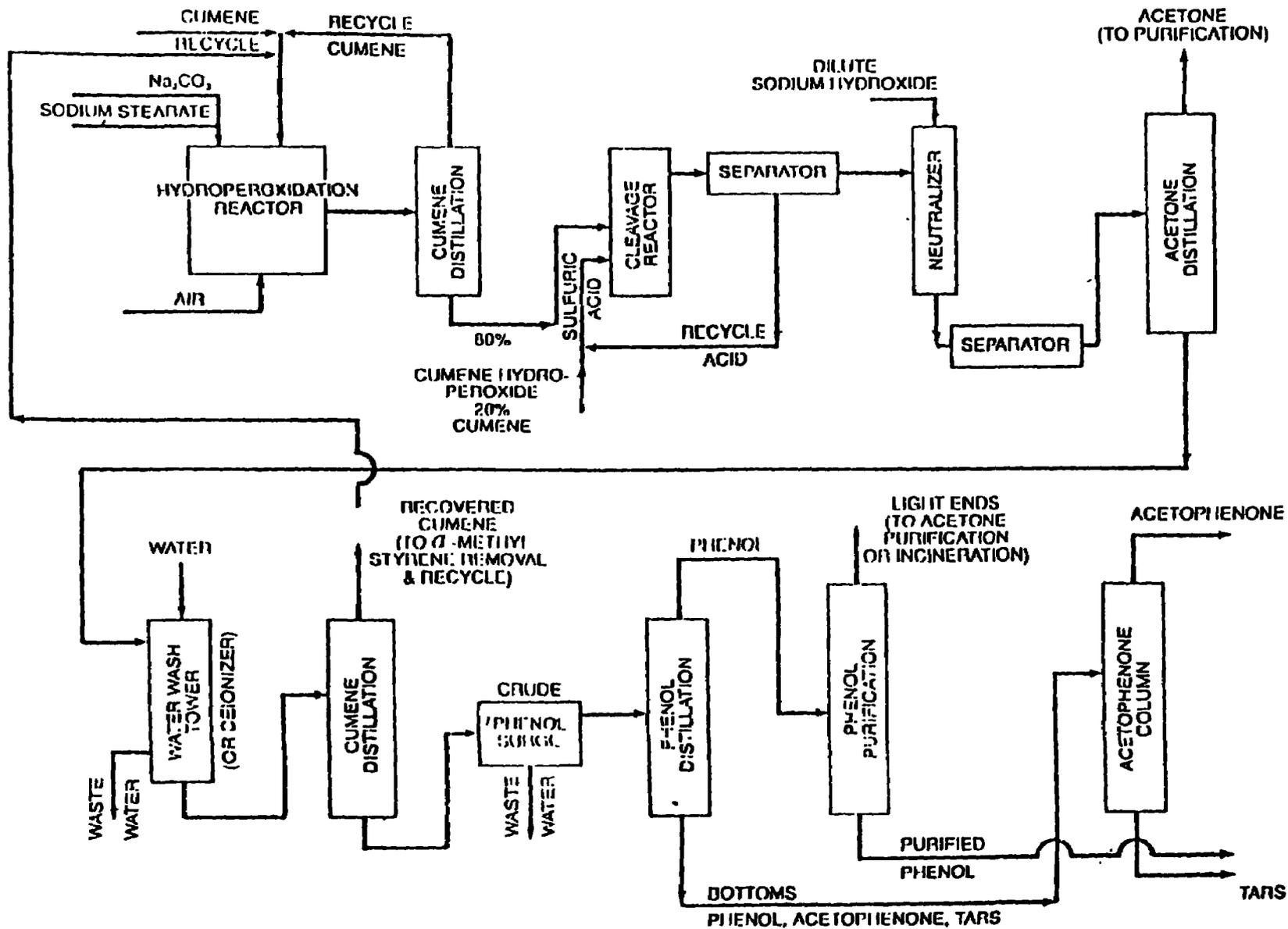


Figure 1. FLOW DIAGRAM—PHENOL/ACETONE FROM CUMENE  
(MODIFIED FROM REFERENCE 13)

resultant aqueous waste stream containing sodium sulfate, sodium phenate, phenol, acetone, and sodium stearate is separated and sent to wastewater treatment.\* The crude, neutralized organic layer is then sent to a series of distillation columns where acetone, cumene, phenol and acetophenone and the solvent are recovered. The first column separates a crude acetone product overhead that is further purified by distillation. The bottoms from the acetone distillation column pass through a water scrubber to remove residual acetone and inorganic salts. They then pass to a series of columns where the lower boiling hydrocarbons, solvents, cumene, and alphas-methyl styrene are successively removed, recovered and sold, or recycled or disposed. The bottoms from the last of the series of columns is crude phenol. It goes to a crude phenol surge where any remaining water is settled out. The crude phenol is refined in the next distillation column from which the purified phenol is removed overhead.

The bottoms from the phenol still contain phenol, acetophenone, cumyl phenol, phenyl di-methyl carbinol, higher boiling phenolic compounds, and polymers. This mixture may be further distilled to recover the acetophenone. The still bottoms remaining at the completion of distillation are the waste streams of concern in this document.

#### C. Waste Generation and Management

The distillation bottoms are a tarry solid in physical

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\*The Agency is not listing this wastewater stream at the present time, but solicits data regarding waste composition and quantity, waste constituent concentrations, and waste management practices.

form. An EPA study (Monsanto Research Study Vol. 6) states that these wastes (i.e, the tars generated at the bottom of the acetophenone distillation column) amount to 50 - 110 g tar/Kg (100-220 lb tar/ton of phenol) of phenol product. The reported analysis and quantification breakdown of this residue is:

Acetophenone	1.9 g/Kg (3.8 lb/ton) phenol
Phenol	0.75 g/Kg (1.5 lb/ton) phenol
Cumyl phenol	0.85 g/Kg (1.7 lb/ton) phenol
Total tars	50 - 110 g/Kg (100-220 lb/ton) phenol

The relative concentrations of the various waste constituents can thus be calculated from these production figures.

As is shown above, the waste tars are expected to contain large concentrations of polycyclic aromatic hydrocarbons for the following reasons. Cumene (the essential feedstock material) is itself an aromatic. In the successive steps of hydroperoxidation and acid cleavage, the aromatic ring can open, and polyaromatic ring structures formed. These are high-boiling substances and will be found in the distillation bottom tars.

The subject bottom tar residue is generally incinerated in combined organic wastes incinerators within plant limits.(2) Plants which do not have incinerators hire contract waste haulers/landfillers.(2)

### III. Discussion of Basis for Listing

#### A. Hazards posed by the Wastes

Based on 1977 product production levels (p. 2), the U.S. production of phenol/acetone from cumene generates an estimated 100-220 million lbs of the subject waste annually. The principal waste

components of concern are phenol and tars.<sup>(3)</sup> Phenol is toxic. The tars are suspect carcinogens due to the presence of polycyclic aromatic hydrocarbons (PAH). These waste constituents are capable of migration from the waste to groundwater. Phenol is extremely soluble (67,000 ppm in water) (App B). PAH's contained in tars are less subject to migration, but are highly persistent. (See p. 8 below.) Actual damage incidents and field measurements confirm predictions that waste constituents are capable of migration, mobility, and persistence. Phenol has been found in ppb and ppm concentrations in leachate from sites such as Love Canal, Story Chemical and La Bounty in Charles City, Iowa.<sup>(13)</sup> Levels some eight times above the proposed water quality criteria were found in runoff 1.5 miles from a disposal site near Byron, Illinois.<sup>(13)\*</sup> Residuals and ppb levels of PAH's have been found in leachate samples from the Wade Site (Chester, PA), Reilly Tar and Chemical Co. (St. Louis Park, MN), and Kin-Buc Landfill (Middlesex, NJ)<sup>(13)</sup>.

The primary means of disposal of residue are landfilling or incineration,<sup>(2)</sup> prior to which the wastes are held temporarily in storage containers. Mismanagement by leakage during transport or storage, improper disposal allowing leaching, or incomplete incinerator combustion may all realistically occur, with resulting high potential to cause serious human health effects and exposure of animals in the area through direct contact and through pollution of surface and groundwater.

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\*The reference to the proposed water quality criteria in the text is not meant to use the proposed standard as a regulatory benchmark, but to indicate qualitatively that phenol may cause a potential hazard if it migrates from the waste in small concentrations.

Thus, disposal in a landfill, even if plastic-lined drums are used, represents a potential hazard due to the leaching of toxic compounds if the landfill is improperly designed or operated (i.e., drums corrode in the presence of even small amounts of water). Landfills may, for example, be sited in areas with highly permeable soils, allowing leachate to migrate to groundwater. Proper leachate control and monitoring may not be in current use, again facilitating leachate migration to groundwater, and resulting in migration to environmental receptors. Storage prior to incineration or off-site disposal could lead to similar hazards as improper landfilling, since improperly stored wastes are capable of leaking and contaminating soil and groundwater.

Transport to off-site disposal sites by contract haulers also could result in mismanagement and environmental insult. Not only could these wastes be mishandled in transit, but (absent of proper regulatory control) there is no assurance that these wastes will arrive at their intended destination. As a result, they may become available to do harm elsewhere.

Mismanagement of incineration operations resulting from improper combustion conditions related to temperature, residence time and mixing, could lead to the release into the atmosphere of vapors containing hazardous products of incomplete combustion, including the waste constituents of concern.

Should waste constituents be released from the management environment, they are likely to persist and reach environmental receptors, as shown by the data presented on p. 6 above. Degradative processes

do not appear to appreciably reduce dangers of exposure. Phenol biodegrades at a moderate rate in surface water and soil, but moves readily (App. B.). Even with persistence of only a few days, the rapid spreading of phenol (due to its very high solubility) could cause widespread damage of the ecosystem and contamination of potable water supplies. A phenol spill accident in Wisconsin resulted in the movement of phenol into groundwater and contamination of well water for more than 1000 ft. from the spill. Phenol poisoning symptoms in humans developed from consumption of the well water.<sup>(5)</sup> Phenols were also implicated in one of the damage incidents mentioned in the principal Congressional report on RCRA, again indicating their likelihood to migrate and persist if mismanaged. (See H. Rep. No. 94-1491, 94th Cong., 2nd Sess., 21.) High local concentrations from indiscriminate dumping could easily exceed the limit. If phenol were to migrate to its limit of solubility, concentration levels would be over 10,000 times the proposed human health water quality criteria, indicating a potential chronic toxicity hazard.\*<sup>(16)</sup>

Tar substances of the subject type generally contain polycyclic aromatic hydrocarbons (PAH) which are classified as priority pollutants. The PAH's are limited in movement, but persistent in the environment.

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\*The reference to the proposed water quality criteria in the text is not meant to use the proposed standard as a regulatory benchmark, but to indicate qualitatively that phenol may cause a substantial hazard if it migrates from the waste in small concentrations.

PAH's are tightly absorbed by fine particles, and so are most likely associated with stream, river, and lake sediments.(15) Aquatic animal and plant species living in these media could suffer serious adverse effects. Furthermore, substantial hazard is associated with exposure to extremely small PAH concentrations (concentrations of PAH estimated to result in additional lifetime cancer risks of 1 in 100,000 at 9.7 ng/l(15)) so that only minute concentrations need migrate to create substantial harm.(15)\*

## B. Health and Ecological Effects

### 1. Tars

Health Effects - Tars containing polycyclic aromatic hydrocarbons,(PAH) are suspected carcinogens and mutagens, as well as being toxic.(15)

Tars, in an oily waste containing petroleum lubricants, are very toxic chemicals. They are absorbed into the body by inhalation, ingestion, and through the skin. The oral LD<sub>50</sub> in animals (dog, rabbit) is 600 mg/kg(6). Long term dermal exposure (1-43 years) to coal tar has been reported to cause malignant tumors on hands, face, and neck of briquette factory workers(7). The U.S.E.P.A. Cancer Assessment Group has recommended 9.7 ng/l total PAH limit for water criteria. The limit was based on animal test data and designed to minimize lifetime cancer risk at a rate below 1 in 100,000(8). The limit might reasonably be expected to be exceeded in cases of inadequate

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\*The reference to the proposed water quality criteria in the text is not meant to use the proposed standard as a regulatory benchmark, but to indicate qualitatively that PAH's may cause a potential hazard if they migrate from the waste in small concentrations.

industrial waste disposal. Polycyclic aromatic hydrocarbons are designated as priority pollutants (acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzofluoranthene, benzo perylene, chrysene, dibenzo(a, h) anthracene, fluorene, indenopyrene, phenathrene, pyrene) under section 307(a) of the CWA. Additional information and specific references on the adverse effects of PAH tars can be found in Appendix A.

Ecological Effects - When small amounts of coal tar were mixed with food and fed to ducks, the toxicologic effect was anemia and extensive liver damage.(9)

Regulations - The NIOSH recommended standard for occupational exposure to tar products shall be controlled so employees are not exposed to substances at a concentration greater than 0.1 mg/m<sup>3</sup> for a ten-hour work shift. PAH's are regulated by the Office of Water and Waste Management of EPA under the Clean Water Act.

Industrial Recognition of Hazard - According to handbook used by industry Sax, Dangerous Properties of Industrial Chemicals, petroleum tar is a recognized carcinogen.

## 2. Phenol

Health Effects - Prolonged exposure to phenol vapors has resulted in human digestive disturbances and skin eruptions(10). Damage to liver and kidneys from this exposure can lead to death.(10) Exposure to phenol can result in chronic and acute poisoning. It can be absorbed into the body by inhalation, ingestion, or through the skin. Phenol is very toxic [oral LD<sub>50</sub> in rats is 414 mg/kg].(11) Additional information and specific references on the adverse effects

of phenol can be found in Appendix A.

Ecological Effects - 5 mg/l phenol is the median lethal toxicity (LC<sub>50</sub>) value for the rainbow trout.<sup>(4)</sup>

Regulatory Recognition of Hazard - OSHA has set a TLV for phenol at 5 ppm. EPA's draft criterion for phenol in ambient water is 3.4 mg/l, and 1.0 mg for those waters which may be subject to chlorination.<sup>(4)</sup> The interim drinking water standard for phenol is 1 ug/l. The aquatic draft criterion for protecting freshwater organisms is 600 ug/l, not to exceed 3,400 ug/l.<sup>(4)</sup>

Industrial Recognition of Hazard - Phenol is listed as a dangerous disaster hazard, according to the handbook, Dangerous Properties of Industrial Chemicals<sup>(10)</sup>.

#### IV. References

1. U.S. Trade Commission. Synthetic organic chemicals. United States production and sales. Washington, DC. 1978.
2. U.S. EPA. Survey reports on atmospheric emissions from the petrochemical industry. V.III. EPA No. 450/337/005C. Research Triangle Park, NC. April, 1974.
3. U.S. EPA. Stuewe, C. Emission control options for the synthetic organic chemicals manufacturing industry, trip report - Allied Chemical Corporation, Frankford, PA. EPA Contract No. 68-02-2577. March, 1977.
4. U.S. EPA. Phenol: Ambient water quality criteria. NTIS PB No. 296 787. 1979
5. Baker, E.L. et al. Phenol poisoning due to contaminated drinking water. Arch. Env. Health pp. 89-94. March-April, 1978.
6. NIOSH. Registry of toxic effects of chemical substances. U.S. Dept. of Health, Education and Welfare. p. 370. January, 1979.
7. Pierre, F., J. Robillard, and A. Mouchel. Skin tumors in workers exposed to coal tar. Arch. Mal. Prof. Med. Trav. Secure. Soc. 26:475-82. 1965.
8. U.S. EPA. Carcinogen Assessment Group. Derivation of the water quality criterion for polycyclic aromatic hydrocarbons. July, 1979.
9. Carlton, W. W. Experimental coal tar poisoning in the white Peking duck. Avian Dis. 10:484-502. 1966.
10. Sax, N. I. Dangerous properties of industrial materials, 4th ed. Van Nostrand Reinhold Co., New York. p. 1008. 1975.
11. U.S. EPA. Multimedia environmental goals for environmental assessment. V.II. EPA No. 600/7-77-1366. November, 1977.
12. National Academy of Sciences, National Academy of Engineering. Water quality criteria 1972. A report, National Academy of Sciences. Washington, DC. EPA No. R3-73-033. 1973.
13. Lowenheim F.A., and M. K. Moran. Faith, Keyes, and Clarke's industrial chemicals, 4th ed. John Wiley and Sons, Inc., New York. 1975.
14. U.S. EPA. Industrial process profiles for environmental use: Chapter 6, The industrial organic chemicals industry. Ralmond Liepins, Forest Nixon, Charles Hudak, and Terry Parsons. EPA No. 600/277-023f. 1977.
15. U.S. EPA. Water quality criteria document, polynuclear aromatic hydrocarbons. NTIS PB No. 297 926.

16. Dawson, English and Petty. Physical chemical properties of hazardous waste constituents. 1980.

Response to Comments - Distillation Bottom Tars from the  
Production of Phenol/Acetone from Cumene

Distillation bottom tars from the production of phenol/acetone from cumene (K022) are listed as hazardous because they contain both phenol and polycyclic aromatic hydrocarbons (PAHs). One commenter objected to the inclusion of phenol as a constituent of concern in this particular listing. The commenter argued that since phenol has not been established as a carcinogen, the compound is not of significant toxicity to be included as a basis for listing. The commenter also pointed out some inconsistencies between the aforementioned listing background document and the Health and Environmental Effects Profile on phenol.

The Agency strongly disagrees with the commenter. While the carcinogenicity of phenol has not been firmly established, both liver and kidney damage to humans will result from the chronic exposure to phenol with death a potential consequence. In addition, the acute toxicity of phenol results in central nervous system (CNS) depression with symptoms severe enough to earn phenol an acute toxicity rating of "high" in Sax.<sup>(10)</sup> This widely accepted reference indicates that "death or permanent injury may occur due to exposure at normal use..." Therefore, the Agency will continue to include phenol as a constituent of concern in this particular listing.\*

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\*It should be noted that the Agency recently determined to retain the listing of phenol as a toxic pollutant under §307(a) of the Clean Water Act. The reasons for that action are incorporated by reference herein.

HAZARDOUS WASTE BACKGROUND DOCUMENT  
PHTHALIC ANHYDRIDE PRODUCTION

Distillation light ends from the production of phthalic anhydride from naphthalene (T)

Distillation bottoms from the production of phthalic anhydride from naphthalene (T)\*

Distillation light ends from the production of phthalic anhydride from ortho-xylene (T)

Distillation bottoms from the production of phthalic anhydride from ortho-xylene (T)\*\*

I. Summary of Basis for Listing

The production of phthalic anhydride via vapor phase oxidation of naphthalene or ortho-xylene results in the generation of distillation residues which contain carcinogens and toxic organic compounds. The residues of concern are the light ends and bottoms which result from the distillation step in which crude phthalic anhydride is purified. The waste constituents of concern are phthalic anhydride, maleic anhydride, and 1,4-naphthoquinone.

\*On May 19, 1980, EPA promulgated in interim final form, "Distillation bottoms from the production of phthalic anhydride from naphthalene" as hazardous because it contains among other things naphthoquinones. In re-evaluating the process chemistry, however, the Agency believes that 1,4-naphthoquinone will be the predominant isomer found in this waste and, thus is modifying the constituent of concern to refer to 1,4-naphthoquinone rather than the general class of naphthoquinones.

\*\*The Agency listed quinones as a hazardous constituent of concern for hazardous waste listing No. K094 (Distillation bottoms from the production of phthalic anhydride from ortho-xylene). In re-evaluating the toxicity of these compounds, the Agency believes that insufficient data is currently available regarding the acute and chronic effects of the higher molecular weight quinones and their derivatives to support designating them as toxic constituents of a waste. The Agency would only expect to find the higher molecular weight quinones in this waste, based on the process chemistry. Therefore, the Agency has removed quinones as a constituent of concern for this waste stream.

With respect to the commenter's concern as to inconsistencies between the listing background document and the Health and Environmental Effects Profile on phenol, the Agency will make the appropriate corrections.

The Administrator has determined that these distillation residues are solid wastes which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA.

This conclusion is based on the following considerations:

- (1) The light ends from both processes contain phthalic anhydride and maleic anhydride while the heavy ends from both processes will contain phthalic anhydride. The heavy bottoms from the naphthalene-based process will also contain 1,4-naphthoquinone.
- (2) Phthalic anhydride, maleic anhydride and 1,4-naphthoquinone are organic toxicants. 1,4-Naphthoquinone and maleic anhydride are also animal carcinogens.
- (3) More than 16 million pounds of the constituents of concern will be generated annually and require disposal as a result of phthalic anhydride production (assuming plants are operating at production capacity).
- (4) Disposal of these wastes in improperly designed or operated landfills could result in substantial hazard via groundwater or surface water exposure pathways. Disposal by incineration, if mismanaged, can result in serious air pollution through release of hazardous vapors, due to incomplete combustion. Transportation of wastes off-site by contract haulers increases the possibility of mismanagement.\*

## II. Sources of Waste and Typical Disposal Practices

### A. Industry Profile

The major use of phthalic anhydride is in the manufacture of plastics, plasticizers, paints and synthetic

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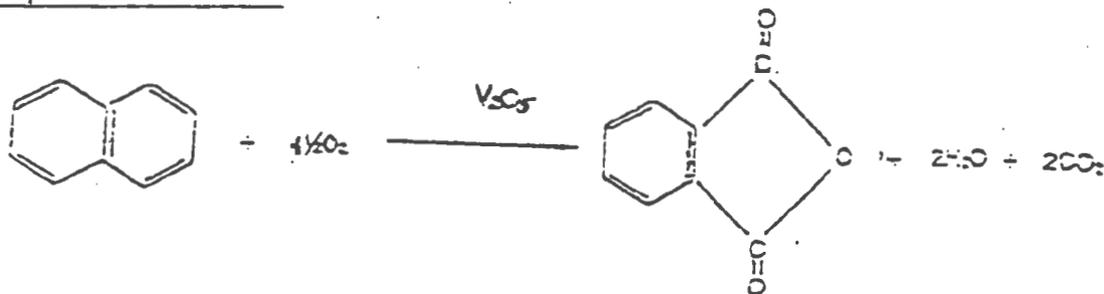
\*Although no data on the corrosivity of these waste streams are currently available, the Agency believes that phthalic anhydride, maleic anhydride and 1,4-naphthoquinone are highly corrosive materials, and that these waste streams may therefore be corrosive. Under §262.11, generators of these waste streams are responsible for determining whether their wastes meet any of the characteristics.

resins (3). Producers of phthalic anhydride from ortho-xylene or naphthalene and the production capacities of these plants are listed in Table 1. About 70% of industry capacity is ortho-xylene-based.

### Manufacturing Process

Phthalic anhydride is manufactured by the vapor phase oxidation of ortho-xylene or naphthalene (see Figures 1 and 2 for flow diagrams). The primary naphthalene-based processes use fluidized bed reactors. All xylene-based processes incorporate tubular fixed bed reactors. Except for the reactors and catalyst handling and recovery facilities required for the fluid unit, these vapor phase processes are similar (3). The two basic reactions are as follows:

#### Napthalene-based



#### NAPHTHALENE

#### Ortho-xylene based



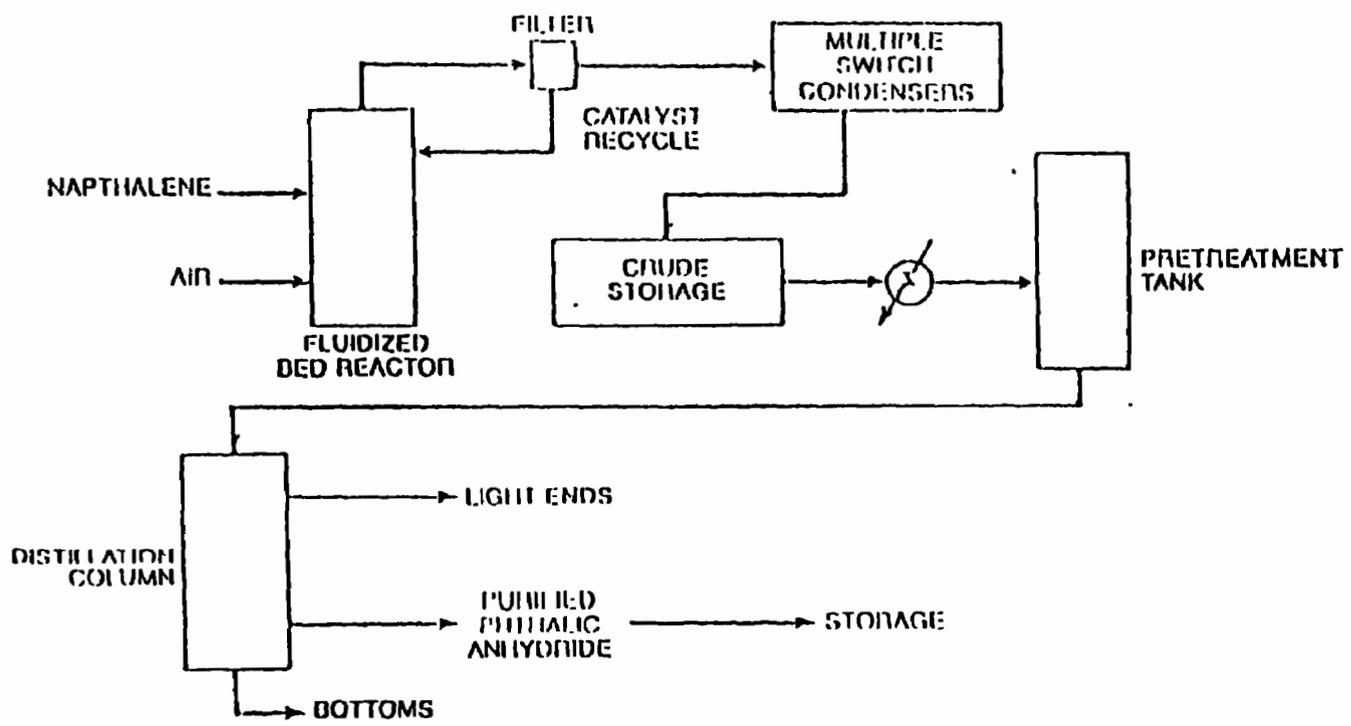
#### PHTHALIC ANHYDRIDE

In the naphthalene-based process, naphthalene is introduced into a fluidized bed reactor near the catalyst bed. In the xylene-based process, o-xylene is mixed with air and introduced into a fixed bed tubular reactor (in which the catalyst is contained in the tubes). Both processes typically use a vanadium

Table 1. Producers of phthalic anhydride

<u>Producer</u>	<u>Location</u>	<u>Annual Capacity (Millions of Pounds)</u>	<u>Raw Material</u>
Allied Chem. Corp. Specialty Chems. Div.	El Segundo, Calif.	36	o-xylene
BASF Wyandotta Corp. Colors and Intermediate Group Intermediates Div.	Kearny, N.J.	150	o-xylene
Exxon Corp. Exxon Chem. Co., div. Exxon Chem. Co. U.S.A.	Baton Rouge, La.	130	o-xylene
Koppers Co., Inc. Organic Materials Group	Bridgeville, Pa.	90	Desulfurized coal-tar naphthalene
	Cicero, Ill.	235	o-xylene or naphthalene
Monsanto Co. Monsanto Chem. Intermediates Co.	Bridgeport, N.J. Texas City, Tex.	85 150	Petroleum naphthalene o-xylene
Occidental Petroleum Corp. Hooker Chem. Corp., subsid. Hooker Chems. and Plastics Corp. subsid. Puerto Rico Chem. Co., subsid.	Arecibo, P.R.	87	o-xylene
Standard Oil Co. of California Chevron Chem. Co., subsid. Petrochem. Div.	Richmond, Calif.	50	o-xylene
Stepan Chem. Co. Surfactant Dept.	Millsdale, Ill.	100	o-xylene
United States Steel Corp. USS Chems., div.	Neville Island, Pa.	205	Desulfurized coal tar naphthalene
		<b>TOTAL</b>	<b>1318</b>

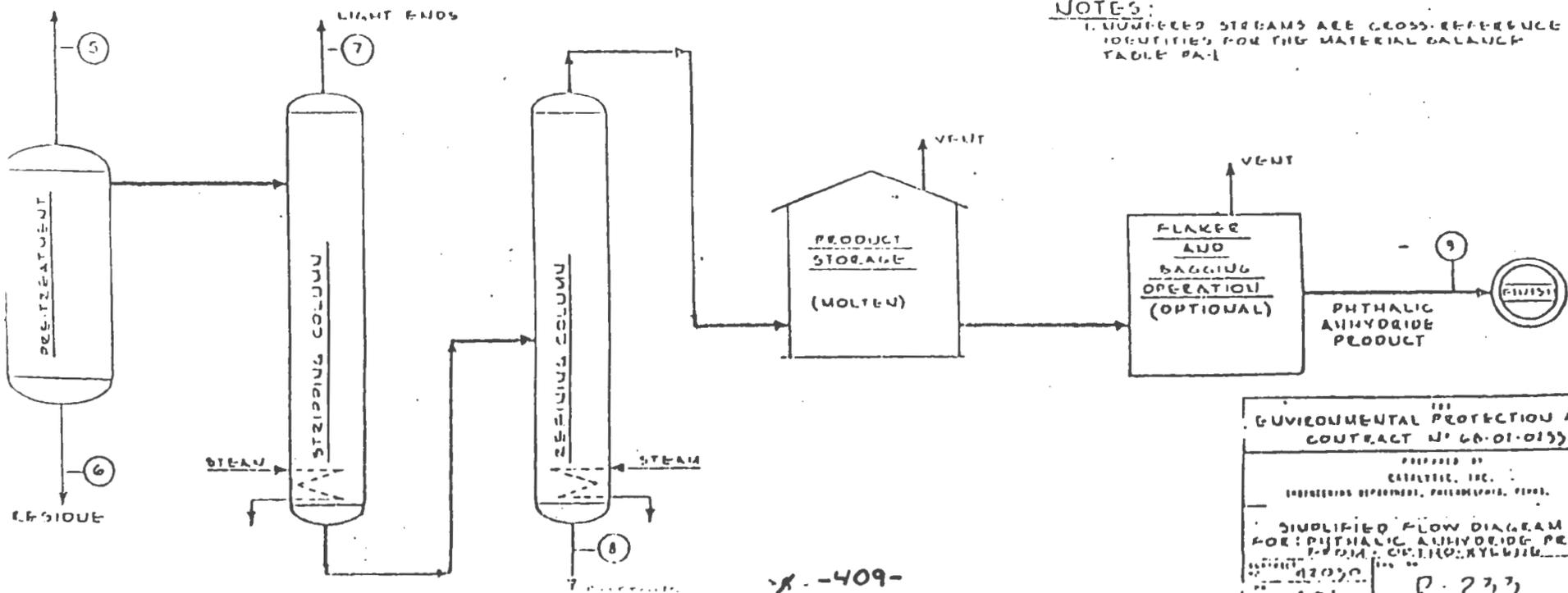
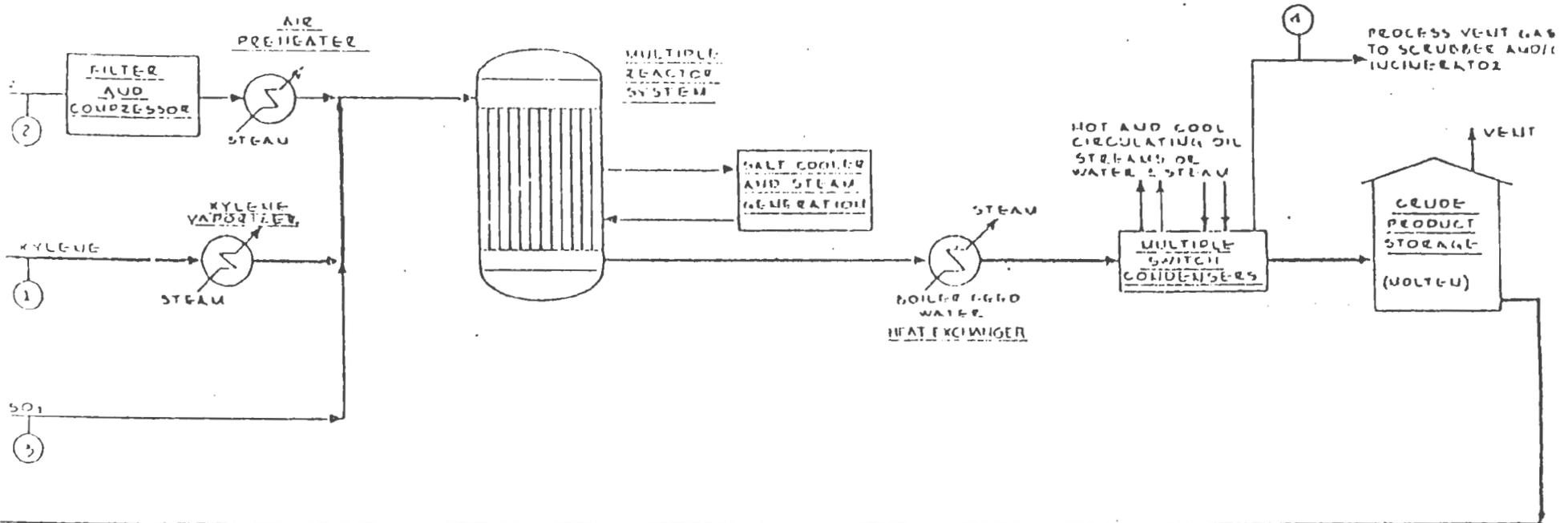
Source: Reference 1



**Figure 1. PHTHALIC ANHYDRIDE PRODUCTION FROM NAPHTHALENE**  
 Source: Reference 3

Figure 2. PHthalic Anhydride Production from ortho-xylene

(Source: reference 3)



NOTES:  
1. NUMBERED STREAMS ARE CROSS-REFERENCE IDENTIFIED FOR THE MATERIAL BALANCE TABLE PA-1

ENVIRONMENTAL PROTECTION AG  
CONTRACT N° 68-01-0133  
PREPARED BY  
CATALYTIC, INC.  
ENGINEERING DEPARTMENT, PHILADELPHIA, PENN.  
SIMPLIFIED FLOW DIAGRAM  
FOR: PHthalic ANHYDRIDE PROC  
FROM: ortho-xylene  
41030 P-233

The reactor effluent from both processes will contain phthalic anhydride, maleic anhydride\*, and miscellaneous organics (including fused-ring compounds). The ortho-xylene based process will generate quinones\*\* as part of its waste stream. The naphthalene-based process will generate naphthoquinones.(3)

Crude phthalic anhydride is condensed by passing through a series of switch condensers. (The condenser effluent gases are normally water scrubbed and/or sent to an incinerator before being released to the atmosphere.) As part of the purification process, the crude product is first distilled to remove light ends. The stripped crude phthalic anhydride is then distilled in a second column where heavy bottoms will remain once the pure product is removed.(3) These distillation residues are the waste streams of concern.

## II. Waste Generation and Management

Some actual plant data describing light ends and bottoms generation are available. One naphthalene-based plant, with a published production capacity of 125 million pounds/year phthalic anhydride, reported to dispose of 58,000 pounds/month of light ends and 400,000 pounds/month of bottoms. This plant had these wastes hauled off-site by a contractor (3), probably for disposal by landfill.

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\*Process chemistry indicates that maleic anhydride will be present in lower concentrations in the effluent generated from ortho-xylene based phthalic anhydride production.

\*\*As indicated earlier, the Agency would only expect to find the higher molecular weight quinones in this waste based on the process chemistry. In re-evaluating the toxicity of these higher molecular weight quinones, we believe that insufficient data is currently available regarding the acute and chronic effects of these compounds; therefore, quinones will not be included as a constituent of concern.

A second naphthalene-based plant, with nominal capacity of 90 million pounds/year, reported a combined total waste load of 45,000 pounds/month. This plant utilized an on-site landfill for solid waste disposal.(3)

One plant using ortho-xylene as a raw material reported a light and heavy ends generation rate of 0.02 tons/ton of phthalic anhydride produced. Another ortho-xylene plant reported that it generated 0.002 tons of distillation bottoms per ton of phthalic anhydride produced. Both plants reported that these wastes are sent off-site for disposal(3).

Based on typical material balance data(3)\*, it can be estimated that the following amounts of the constituents of concern will be contained in the distillation residues generated as a result of total phthalic anhydride production (assuming all plants are operating at production capacity):

<u>Constituent</u>	<u>Amount from xylene-based production</u> (million lbs./yr.)		<u>Amount from Napthalene-based</u> (million lbs./yr.)	
	<u>light ends</u>	<u>heavy bottoms</u>	<u>light ends</u>	<u>heavy bottoms</u>
phthalic anhydride	>4.9	>0.9	>0.2	>2.5
maleic anhydride	**		>1.9	
1,4-naphthoquinone				>2.5

\*Estimates based on typical material balance data for average plants producing 130 million lbs./yr of phthalic anhydride from ortho-xylene and from naphthalene. Source: reference 3.

\*\*Process chemistry indicates that maleic anhydride will be present in lower concentrations in the light ends generated from phthalic anhydride production from ortho-xylene than from naphthalene, due to the nature of the basic chemical reactions.

Disposal practices for distillation residues will vary. Light ends, either in a vapor or liquid state, are usually incinerated. However, as noted above, one plant reported having this waste, along with the heavy ends, hauled off-site by a contractor<sup>(3)</sup>, probably to a landfill disposal site. Distillation bottoms may also be incinerated, but are typically disposed of in landfills either on or off-site.<sup>(3)</sup>

### III. Discussion of Basis for Listing

#### A. Hazards Posed by the Waste

As noted above, distillation residues (light ends and heavy bottoms) from phthalic anhydride production contain the following components as they are discharged from the plant distillation units:

Phthalic anhydride  
Maleic anhydride \*  
1,4-Naphthoquinone

All of the above waste constituents are toxic. 1,4-Naphthoquinone and maleic anhydride are also demonstrated carcinogens.

These waste constituents appear capable of migration, mobility and persistence if mismanaged, creating the potential for substantial hazard in light of the dangers associated with contact with the waste constituents. As previously noted, disposal of these wastes may be by incineration, on-site landfilling,

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\*Maleic anhydride, while an animal carcinogen, hydrolyzes and photolyzes rapidly to non-toxic maleic acid and thus is not expected to pose a hazard via a water or air exposure pathway. It may, however, prove hazardous during waste transport to off-site disposal.

or off-site disposal (probably a landfill). Improper design and management of land disposal facilities could lead to the release of hazardous constituents and pose a hazard via a groundwater exposure pathway. Some of the waste constituents have in fact proved capable of migration, mobility and persistence via this pathway. For example, phthalic anhydride has been identified in finished drinking water.(14)

1,4-Naphthoquinone is relatively soluble (about 200 mg/l), and thus may also migrate from the matrix of the waste.

Disposal by incineration, if mismanaged, can present a health hazard via an air inhalation pathway. Incomplete combustion of the distillation residues from phthalic anhydride production can result in the formation of various phthalate esters which will be released from the incinerator into the air. (These esters would be formed from the reaction of phthalic acid with alcohols.) Certain phthalates have shown mutagenic effects. Phthalates have also been shown to produce teratogenic effects in rats. Chronic toxicity includes toxic polyneuritis in workers exposed primarily to dibutyl phthalate (see Appendix A).

Contract hauling, in particular, presents an additional potential for mismanagement in the transportation and handling operations. Transportation of these wastes off-site, if not properly managed, increases the likelihood of their causing harm to human health and the environment. The mismanagement of wastes during transportation thus may result in hazard to human health

and wildlife through direct exposure to the harmful constituents listed above (either by direct contact with the waste or through wind-carried particulate matter and vapors). Furthermore, absent proper management safeguards, the wastes might not reach the designated destination at all, thus making them available to do harm elsewhere. It should be noted that maleic anhydride, which is not otherwise a constituent of concern due to its lack of persistence, could prove hazardous during transport and handling, since the possibility of immediate exposure exists.

The large quantity of waste generated and requiring disposal is another factor which increases the likelihood of exposure to the harmful constituents in the waste via the various exposure pathways. Should the large amounts of waste constituents exposed to leaching activity be released as a result of mismanagement, large areas of ground and surface waters may be affected. Contamination could also occur for long periods of time, since large amounts of pollutants are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or used up due to the large quantities of pollutants available over long periods of time. All of these considerations, in the Agency's view, strongly support a hazardous waste listing.

B. Health and Ecological Effects

1. Maleic Anhydride

Health Effects - Maleic anhydride can produce cancers following subcutaneous injections in rats.(5) Maleic anhydride is also highly toxic [ORAL rat LD50 = 481 mg/Kg] and is known to cause acute irritation of the eyes, skin and upper respiratory tract. There is also evidence that this compound may cause reproductive impairment in male rats (4). Additional information and specific references on the adverse health effects of maleic anhydride can be found in Appendix A.

Regulations - OSHA has set a standard for air of TWA at 0.25 ppm for an 8-hour day.(7)

Industrial Recognition of Hazard - In Sax, Dangerous Properties of Industrial Materials, Maleic anhydride is designated as highly toxic by ingestion, and also as an irritant. Fassett and Irish in Industrial Hygiene and Toxicology state that maleic anhydride can produce severe eye and skin burns. Plunkett, in his Handbook of Industrial Toxicology designates maleic anhydride as a causal agent of severe eye and skin burns.

2. Phthalic Anhydride

Health Effects - There is evidence that phthalic anhydride may act as a teratogen in chick embryos(6). It is a potent irritant of the skin, eyes, and upper respiratory tract. Exposure has been reported to produce progressive respiratory damage, including fibroses of the lungs(8,9). In addition, degeneration of liver, kidney and myocardium

occured(6). There is also evidence that this compound may cause reproductive impairment in male rats(4). Additional information and specific references on the adverse effects of phthalic anhydride can be found in Appendix A.

Regulations - OSHA has set a TWA for an 8-hour exposure at 2 ppm.(7)

Industrial Recognition of Hazard - Sax (Dangerous Properties of Industrial Materials) lists phthalic anhydride as having a moderate toxic hazard rating via oral routes.

### 3. 1,4-Naphthoquinone

Health Effects - 1,4-Naphthoquinone has been demonstrated to be a carcinogen when applied to the skin of test animals(5). This chemical is extremely irritating to the skin, mucous membranes and respiratory tract. It can cause skin and pulmonary sensitization resulting in asthmatic and allergic responses. Changes in the blood that reduce its oxygen carrying capacity have also been demonstrated following 1,4-naphthoquinone exposure which may develop into hemolytic anemia. 1,4-Napthoquinone is also suspected of causing adverse reproductive effects. Additional information and specific references on the adverse effects of 1,4-naphthoquinone can be found in Appendix A.

Ecological Effects - Naphthoquinone, at a concentration of 1.0 mg/l will cause death within 3 hours for bluegill and trout, and 14 hours for larval lamprey (10).

Industrial Recognition of Hazard - 1,4-Naphthoquinone is designated in Sax's Dangerous Properties of Industrial Materials as a moderately toxic irritant to skin, eyes, and the upper respiratory tract.

#### IV. References

1. Stanford Research Institute. Directory of chemical producers-United States. SRI International, Menlo Park, CA. 1979.
2. Not used in text.
3. U.S. EPA. Office of Air Quality Planning and Standards. Engineering and cost study of air pollution control for the petrochemical industry, V.7: Phthalic anhydride manufacture from ortho-xylene. Research Triangle Park, North Carolina. EPA No. 450/3-73-006g. NTIS PB No. 245 277. July, 1975.
4. Protsenko, E.I. Gonadotropic action of phthalic anhydride. Gig. Sanit. 35:105. 1970.
5. NIOSH. Registry of toxic effects of chemical substances. U.S. Dept. of Health, Education, and Welfare. 1979.
6. U.S. EPA. Preliminary environmental hazard assessment of chlorinated naphthalenes, silicones, fluorocarbons, benzenepolycarboxylates and chlorophenols. Syracuse University Research Corporation, NTIS PB No. 238 074. 1973.
7. American Conference of Governmental Industrial Hygienists. Documentation of threshold limit values for substances in workroom air, 3rd Edition. 1971.
8. Markman and Savinkina. The condition of the lungs of workers in phthalic anhydride production (an X-ray study). Kemerovo 35. 1964.
9. Plunkett, E.R. Handbook of industrial toxicology. pg. 338.
10. Applegate, V.C., J.H. Howell, and A.E. Hall, Jr. Toxicity of 4,346 chemicals to larval lampreys and fishes. Department of Interior, Special Scientific Report Number 207. 1957.
11. Not used in text.
12. Not used in text.
13. Not used in text.
14. U.S. EPA. Shackelford and Keith. Frequency of organic compounds identified in water. Environmental Research Laboratory. Athens, GA. EPA No. 600/4-76-062. NTIS PB No. 265 470. December, 1976.

Response to Comments - Distillation Light Ends and Bottoms  
from the Production of Phthalic Anhydride from Naphthalene

One commenter raised several questions with respect to wastes K023 and K024 (Distillation light ends and bottoms from the production of phthalic anhydride from naphthalene).

1. The commenter first argued that inclusion of wastes from the production of phthalic anhydride appear to be based generally on the nature of known acute hazards from the pure or technical grade components of chemicals found in the waste rather than the toxicity of the waste itself, i.e., the commenter indicated that the actual waste contains considerable amounts of inert materials rejected from the process. Additionally, the commenter felt that the listing background document did not adequately address the solubility and actual hazards of the waste. Needing an explanation of this particular comment, the Agency contacted the commenter and requested further clarification. The commenter indicated that the hazardousness of the waste should be determined by taking a representative sample of the waste, applying the extraction procedure (EP), and the decision as to whether the waste is hazardous be based on the results of the EP test".

The commenter quite simply misperceives the separate regulatory mechanisms of identifying hazardous wastes through individual listings or through characteristics. (This distinction is explained in detail

in the preamble to Part 261 and in the Background Documents concerning the Criteria for Listing and the EP Toxicity Characteristic.) In initially developing the toxicity characteristic, the Agency intended the extraction procedure (EP) to identify toxic contaminants other than those specified in the National Interim Primary Drinking Water Standards (NIPDWS). However, the Agency was unable to do this, because no other chronic exposure threshold levels relating to drinking water consumption have been established for other contaminants. More importantly, the Agency was not fully confident that it could suitably define and construct testing protocols to accurately assess the hazards presented by these other toxic contaminants. Therefore, the Agency presently has decided to regulate wastes containing non-drinking water standard contaminants through the listing process.

The criteria for listing toxic wastes are intended by EPA to identify all those wastes which are toxic, carcinogenic, mutagenic, teratogenic, phytotoxic or toxic to aquatic species. These criteria provide that a waste will be listed where it contains any of a number of designated toxic constituents-unless, after consideration of certain specified factors (see §261.11(a)(3) for list of factors), the Agency concludes that the waste does not meet Part B of the statutory definition of hazardous waste.

The Agency has adopted this flexible, multiple factor approach to listing toxic wastes rather than the formulaic approach embodied in the characteristics because it considers this approach to be better able to accommodate itself to complex determinations of hazard. EPA further believes that this multiple factor approach was to some extent contemplated by Congress (see the preamble to the Part 261 regulations for a more detailed discussion).

In using this approach, the Agency has listed both distillation light ends and bottoms from the production of phthalic anhydride from naphthalene as hazardous because: (1) these wastes contain a number of toxic constituents which have been identified by the Agency (i.e., phthalic anhydride, maleic anhydride and 1,4-naphthoquinones. and (2) after considering a number of the factors specified in §261.11(a)(3) including the toxicity presented by the constituents, the capability of the toxic constituents in the waste to migrate from the waste and be mobile and persistent in the environment, the quantities of toxic contaminants generated in the waste, plausible types of improper management to which the waste could be subjected, etc., the Agency believes that these wastes, if improperly managed, could present a substantial hazard to human health or the environment. However, it should be noted that one of the constituents of concern, tars, has been removed as a basis for listing.

In re-evaluating the toxicity of these chemical tars, the Agency believes that insufficient data is currently available to consider chemical tars as suspect carcinogens (i.e., all the data on the carcinogenicity of these tars is on coal tars not chemical tars). Therefore, the listings distillation light ends and bottoms from the production of phthalic anhydride from naphthalene have been amended to remove tars as a constituent of concern.

- (2) The commenter then argued that wastes which are properly managed (i.e., by incineration) should not be classified as hazardous because, incineration is a proper management technique. In defining a hazardous waste, the Agency has attempted to reach those wastes which are hazardous if mismanaged under some likely mismanagement scenario. This of course is what the statute requires, see Section 1004(5) of RCRA. The purpose of this definition is to bring these wastes into the hazardous waste management system set up by Sections 3002 through 3005 of RCRA--not to specify management practices. If management practices were made part of the definition so that properly managed wastes were excluded from the definition, the effectiveness of the management system created under Sections 3002 through 3005 might well be vitiated, since properly managed wastes would be excluded at the outset from the

continuing supervision and control provided by the management system thus prejudicing the Agency's ability to ensure continued compliance with these proper management practices. The regulations promulgated under §§3004 and 3005 on May 19, 1980 (45 FR 33154-33588), and those to be promulgated in the future will be sufficiently flexible to accommodate wastes which are properly managed and allow these facilities to continue their present operations.

Based on the foregoing discussion, the Agency will continue to list wastes K023 and K024 (Distillation light ends and bottoms from the production of phthalic anhydride from naphthalene) as hazardous.

## LISTING BACKGROUND DOCUMENT

### NITROBENZENE PRODUCTION

- ° Distillation bottoms from the production of nitrobenzene by the nitration of benzene (T)

#### I. Summary of Basis for Listing

Distillation bottoms from the production of purified nitrobenzene by the nitration of benzene contain carcinogenic, mutagenic, and toxic organic substances. These include meta-dinitrobenzene and 2,4-dinitrotoluene as the pollutants of concern.

The Administrator has determined that the distillation bottoms from nitrobenzene production by the nitration of benzene may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise mismanaged, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- 1) The waste contains meta-dinitrobenzene which is extremely toxic and 2,4-dinitrotoluene, a carcinogen and mutagen.
- 2) The distillation bottoms from the distillation of nitrobenzene are currently disposed of in drums in private landfills. However, these drums have a limited life-time and eventual rupture is likely. When this occurs, the potential for ground water contamination is high if the landfill is not properly designed or operated. Such nitrobenzene accidents have actually occurred.
- 3) The wastes in this stream biodegrade very slowly, thereby increasing the chances for exposure and posing a risk to humans.

#### II. Sources of Waste and Typical Disposal Practices

##### A. Profile of the Industry

The major use of nitrobenzene ( $C_6H_5NO_2$ ) (about 97%) is as an intermediate in the manufacture of aniline dyes.<sup>(1)</sup>

The balance is purified for use chiefly as a solvent or in the manufac-

ture of pharmaceuticals. Nitrobenzene is manufactured in seven plants, all located in the eastern and southern regions of the U.S. Table 1 lists these plants and their production capacities.

TABLE 1. Nitrobenzene Producer Locations and Production Capacities(2)

<u>Company</u>	<u>Facility</u>	<u>1978 Production Capacity (Gg)*</u>
American Cyanamid Co. Organic Chems Div.	Bound Brook, NJ	48
E.I. DuPont deNemours & Co., Inc.	Willow Island, WV	33
Chems. Dyes and Pigments Dept.	Beaumont, TX	140
Indust. Chems. Dept.	Gibbstown, NJ	90
First Mississippi Corp. First Chem. Corp., Subsid.	Pascagoula, MS	151
Mobay Chem. Corp. Polyurethane Div.	New Martinsville, WV	61
Rubicon Chems., Inc.	Geismar, LA	<u>34</u>
	TOTAL	557**

\*Gg = billion grams or 1000 metric tons (mt).  
mt = 2,200 pounds.

\*\*The 1978 U.S. production of nitrobenzene by the nitration of benzene was 260 (10<sup>3</sup>) mt.(2)

The production of nitrobenzene has been fairly stable and can be expected to grow in relation to the growth in demand for aniline production that requires nitrobenzene as a feedstock.

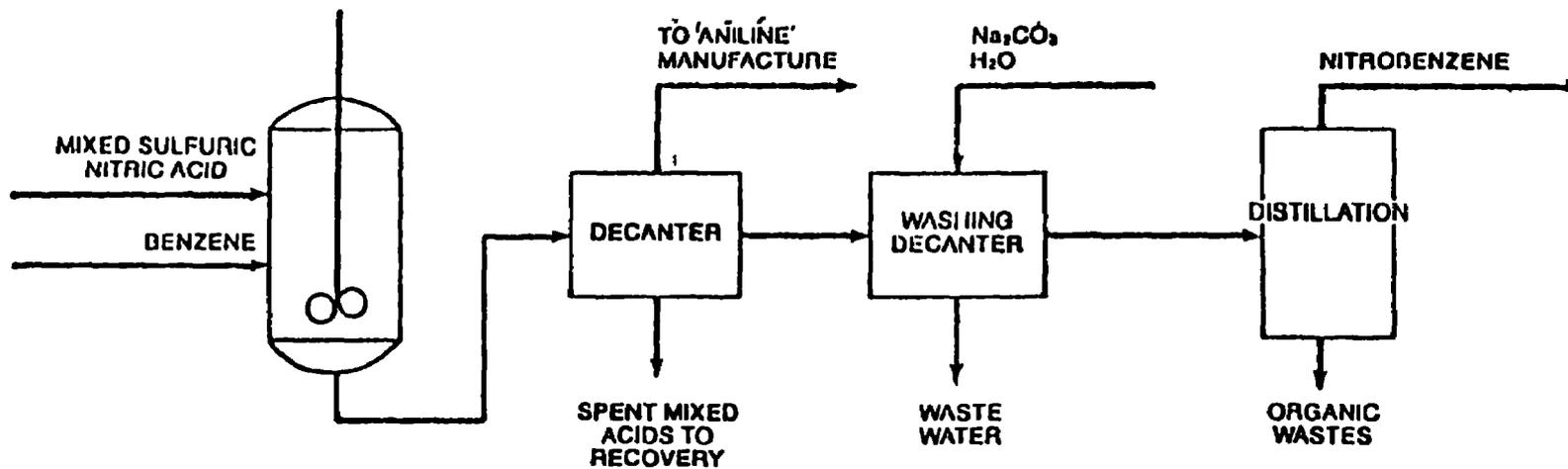
Based on a total nitrobenzene production of 260 Gg/yr (286,000 tons), the amount of nitrobenzene subject to purification by distillation is 3% of production, or 7.8 Gg/yr (8580 tons).(22)

#### B. Manufacturing Process (21)

Nitrobenzene is made by the direct nitration of benzene using a sulfuric-nitric acid mixture (Fig. 1). Commercial specification for the benzene raw material is:

Benzene	99.8%
Toluene	0.1% Maximum
Saturated hydrocarbons	0.1% Maximum
Thiophene	1 ppm

Benzene is added to a slight excess of the sulfuric-nitric acid mixture (53-60% sulfuric acid; 32-39% nitric acid; 8% water; a stoichiometric excess of nitric acid is used) slowly with agitation and heat removal. The reaction residence time is 2-4 hours. At the end of this time, the mixture is allowed to settle and the crude nitrobenzene is withdrawn; the separated, mixed acids (mostly sulfuric) are then sent to acid recovery and reused. The small amount of organic material contained in this stream is recovered from the acid concentration plant and recycled. The crude nitrobenzene is first washed with dilute sodium carbonate solution to neutralize acids, then distilled. The nitrobenzene is recovered as an overhead product. Distillation bottoms, the listed waste stream, are then disposed of as waste.



**Figure 1. FLOW DIAGRAM  
NITRATION OF BENZENE**

(Modified from (21))

C. Waste Generation and Management

The distillation bottoms are deemed to consist primarily of nitrobenzene, meta-dinitrobenzene, and 2,4-dinitrotoluene. Meta-dinitrobenzene and 2,4-dinitrotoluene are the waste constituents of concern.

2,4-Dinitrotoluene is predicted to be present from the nitration of impurities in feedstock benzene, chiefly toluene (0.1%) and paraffinic hydrocarbons of the C<sub>6</sub> to C<sub>8</sub> range (0.1%). (See p. 3, above).

Meta-dinitrobenzene is predicted to result from the dinitration of benzene feedstock. Based upon reaction and equilibrium chemistry, it is estimated that approximately 2-3% of the benzene feedstock will produce dinitrobenzene.

The potential amounts of carcinogenic and/or toxic chemicals that will be in the waste from the distillation of 7.8 Gg/yr of crude nitrobenzene (p. 3) are estimated to be:

meta-dinitrobenzene	156-195 mt/yr
2,4-dinitrotoluene	<u>10 mt/yr</u>
Total	166-205 mt/yr*

The usual disposal method of the subject distillation bottoms that cannot be recovered or used directly as a chemical intermediate is disposal in drums in private landfills.(3)

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\*These estimates assume that all contaminants will be separated from the product by distillation, and consequently will all be present in the waste.

### III. Discussion of Basis for Listing

#### A. Hazards Posed by Waste

As stated above, the constituents of concern in this waste are meta-dinitrobenzene, an acutely toxic compound, and 2-4-dinitrotoluene a carcinogen and mutagen. Both of these constituents are estimated to be present in substantial concentrations, and to be generated in large quantities annually. This information itself is sufficient to warrant hazardous waste listing, in light of the danger posed by the waste constituents\*, unless it can be demonstrated that the waste constituents will not migrate and come in contact with environmental receptors.

No such assurance appears possible, as both waste constituents are projected to have migratory potential and to be mobile and persistent in ground and surface water (App. B), so that they can create a substantial hazard if disposal landfills are not properly designed and operated. Thus, meta-dinitrobenzene, which is highly water soluble (3000 ppm), can migrate without degradation through unsaturated sandy soils, and resist degradation in ground and surface waters (App. B).\*\* 2,4-Dinitrotoluene is also highly soluble (2000 ppm in water), and has been demonstrated to migrate through unsaturated sandy soil, and to be persistent in the environment. (App B).

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\*For example, it is Agency policy that there is no safe exposure level for carcinogens, i.e., a single dose in any concentration being sufficient to cause cancer in some part of the exposed population.

\*\*For example, meta-dinitrobenzene has been demonstrated to be only slowly biodegradable in a synthetically prepared sewage effluent.<sup>(4,5,6)</sup>

If the wastes are landfilled, even in plastic-lined drums, they create a potential hazard. All drums have a limited life span, for the exterior metal corrodes in the presence of even small amounts of moisture. When this occurs the potential for groundwater contamination is high if the landfill is not properly designed or operated. It should be noted that all of the subject production facilities are located in regions of significant rainfall (Gulf Coast, NJ, WV), so that ample percolating liquid is available for leachate formation. (In any case, there is no reason to believe that wastes will be containerized at all, since, absent Subtitle C regulation, wastes could be landfilled in a variety of improper ways.)

Nitrobenzenes have in fact migrated from landfills, persisted in and contaminated groundwater in actual waste management practice. Nitrobenzenes and other wastes from a Monsanto Chemical dump migrated into and caused contamination of groundwater in E. St. Louis, Illinois.\* At the La Bounty dump along the Cedar River in Charles City, Iowa, 130,000 kg of nitrobenzenes were disposed of along with several other chemicals. Groundwater collected between the La Bounty dump and the Cedar River contained considerable concentrations of the chemicals including nitrobenzenes.\*

These waste constituents, therefore, are capable of migrating from improperly designed and operated landfills, and reaching environmental receptors. Drumming of these wastes, as occurs in actual prac-

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\*OSW Hazardous Waste Division, Hazardous Waste Incidents, Unpublished, Open File, 1978.

tice, is not an adequate precaution as demonstrated by the Love Canal incident, among others.

These wastes may also create a substantial hazard via a surface water exposure pathway. Should the disposal site be flooded and the wastes come into contact with the surface water, the nitrobenzenes and nitrotoluenes will resist evaporation due to their weight relative to air and their low vapor pressure. As they are also soluble and only slowly degradable (App. B), they have the potential for widespread exposure should surface waters become contaminated.

## B. Health and Ecological Effects

### 1. Meta-dinitrobenzene

Health Effects - Meta-dinitrobenzene is extremely toxic [LD<sub>50</sub> rat 30mg/Kg.] acting as a potent methemoglobin-forming agent, i.e., an agent that reduces the oxygen-carrying capacity of the blood, a condition that can rapidly lead to death.<sup>(7)</sup> Meta-dinitrobenzene can also cause liver damage, serious visual disturbances, and severe anemia, as well as a variety of central nervous system and gastrointestinal symptoms.<sup>(7)(8)</sup> Meta-dinitrobenzene can be stored in body fat. Exposure to sunlight or ingestion of alcohol may potentiate or increase the adverse effects of poisoning.<sup>(7)</sup> Meta-dinitrobenzene is designated as a priority pollutant under Section 307(a) of the CWA. Additional information on the adverse effects of meta-dinitrobenzene can be found in Appendix A.

Ecological Effects - Concentrations of from 2 to 12 mg/l of unspecified isomers of dinitrobenzene have been reported lethal to fish.<sup>(9)(10)</sup> Meta-dinitrobenzene has been shown to inhibit photosynthesis in algae.<sup>(7)</sup>

Regulatory Recognition of Hazard - OSHA has set the TWA for dinitrobenzene at 0.15 ppm. Dinitrobenzene is regulated by the Office of Water and Waste Management of EPA under the Clean Water Act, Section 311. Technical assistance has been requested to obtain data on environmental effects, high-volume production, and spill reports.

Industrial Recognition of Hazard - According to handbooks used by industry such as, Sax, Dangerous Properties of Industrial Chemicals,<sup>(12)</sup> the oral toxic hazard rating is high for dinitrobenzene. When heated, it is dangerous, decomposing to emit toxic fumes; it also possesses an explosion hazard. According to Plunkett, Handbook of Industrial Toxicology,<sup>(8)</sup> m-dinitrobenzene is extremely toxic by oral, inhalation, and percutaneous routes. According to Patty, Industrial Toxicology,<sup>(13)</sup> m-dinitrobenzene is highly toxic.

## 2. 2,4-Dinitrotoluene

Health Effects This compound has been shown to be a carcinogen<sup>(14)(15)</sup> and a mutagen.<sup>(16,17)</sup> 2,4-Dinitrotoluene also causes a decrease in sperm production and atrophy of the testes.<sup>(14,15)</sup>

2,4-Dinitrotoluene is very toxic [LD<sub>50</sub> (rat) - 268 mg/Kg]. Effects of exposure include methemoglobinemia followed by cyanosis, liver damage, anemia and other abnormalities of the blood and effects on the central nervous system and digestive tract. Dinitrotoluene is also an irritant and an allergen. Alcohol produces a synergistic or aggravated effect on the toxicity.<sup>(18,19)</sup> 2,4-Dinitrotoluene is designated as a priority pollutant under Section 307(a) of the CWA. Additional information on the adverse effects of 2,4-dinitrotoluene can be found in Appendix A.

Ecological Effects - An aquatic toxicity for 2,4-dinitrotoluene of 10-100 ppm has been established(20).

Regulatory Recognition of Hazard OSHA has set the TWA for 2,4-dinitrotoluene in air at 1500 micro-g/m<sup>3</sup> (skin).

Industrial Recognition of Hazard - According to handbooks used by industry, such as Sax, Dangerous Properties of Industrial Materials(12), the oral toxic hazard rating for 2,4-dinitrotoluene is very high.

#### IV. References

1. U.S. EPA. Assessment of industrial hazardous waste practices: Organic chemicals, pesticides, and explosives industries. EPA No. 530/SW-118C. NTIS PB No. 251 307. January, 1976.
2. Stanford Research Institute. 1979 Directory of chemical producers-U.S.A. SRI International, Menlo Park, CA. 1979.
3. U.S. EPA. Recommended methods of reduction, neutralization, recovery, or disposal of hazardous wastes, V. XI: Industrial and municipal disposal candidate waste stream constituent profile reports, organic compounds (continued). EPA No. 670/2-73-053-k. NTIS PB No. 224 590. August 1973.
4. U.S. EPA. Bernhard, E.L., and G.R. Campbell. The effects of chlorination on selected organic chemicals. U.S. Environmental Protection Agency. NTIS PB No. 211 160. 1972.
5. G. Bringmann and R. Kuehn. Biological decomposition of nitrotoluenes and nitrobenzenes by *Azotobacter agilis*. Gesundh. Ing. 92(9):273-276. 1971.
6. Allen, L.A. The effect of nitro-compounds and some other substances on production of hydrogen sulfide by sulfate-reducing bacteria in sewage. Proc. Soc. Appl. Bact. (2):26-38. 1949.
7. U.S. EPA. Investigation of selected potential environmental contaminants: Nitroaromatics. NTIS PB No. 275 078. 1976.
8. Plunkett, E.R. Handbook of Industrial Toxicology.
9. McKee and Wolf. Water quality criteria. The Resource Agency of California, State Water Quality Control Board. Publication No. 3-4. 1963.
10. Meinck, et al. Industrial waste water, 2nd ed. Gustav Fisher Verlag Stugart. p. 536. 1956.
11. Not used in text.
12. Sax, N.I. Dangerous properties of industrial materials, 4th ed. Van Nostrand Reinhold Company, New York. 1975.
13. Patty, F.A. Industrial hygiene and toxicology. G.D. Clayton and F.E. Clayton, eds. 3rd rev. Wiley Publications, New York. 1978.
14. Purchase, I.F.H., et al. An evaluation of 6 short-term tests for detecting organic chemical carcinogens. Br. J. Cancer 37:873-958. 1978.

15. National Cancer Institute. Bioassay of 2,4-dinitrotoluene for possible carcinogenicity. U.S. Department of Health, Education and Welfare, Public Health Service, National Institute of Health. NTIS PB No. 280 990. 1978.
16. Won, W.D., et al. Mutagenicity studies on 2,4-dinitrotoluene. Mutat. Res. 38:387. 1976.
17. Hodgson, J.R., et al. Mutagenicity studies on 2,4-dinitrotoluene. Mutat. Res. 38:387. 1976.
18. Friedlander, A. On the clinical picture of poisoning with benzene and toluene derivatives with special reference to the so-called anilinism. Neurol. Zentrabl. 19:155. 1900.
19. McGee, L.C., et al. Metabolic disturbances in workers exposed to dinitrotoluene. Am. Jour. Dig. Dis. 9:329. 1942.
20. NIOSH. Registry of toxic effects of chemical substances. 1976 ed.
21. Lowenheim F. A., and M. K. Moran. Faith, Keyes and Clark's industrial chemicals, 4th ed. New York. 1975.
22. U.S. International Tariff Commission. Synthetic organic chemicals U.S. production and sale. 1978.

LISTING BACKGROUND DOCUMENT  
METHYL ETHYL PYRIDINE PRODUCTION

Stripping Still Tails from the Production of Methyl  
Ethyl Pyridine (T)

I. SUMMARY OF BASIS FOR LISTING

This waste consists of the stripping still tails generated in the production of methyl ethyl pyridine. The waste is expected to contain toxic organic materials -- paraldehyde, pyridine(s), and picoline(s) -- based on a review of the process involved. The Administrator has determined that this is a solid waste which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to management controls under Subtitle C of RCRA. This conclusion is based on the following considerations:

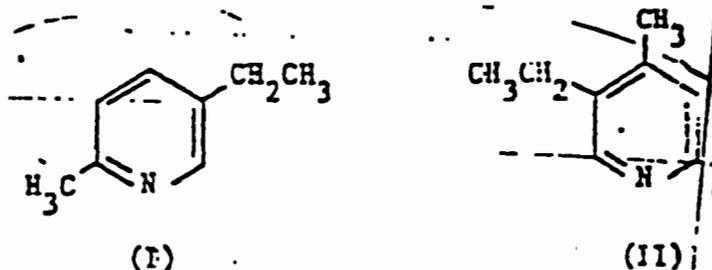
- 1) The waste is expected to contain the following toxic organic chemicals: paraldehyde, pyridines, and picolines. Paraldehyde is included on the NIOSH list of suspected carcinogens. The constituents also exhibit human and aquatic toxicity.
- 2) The constituents in the waste could migrate to groundwater by leaching from improperly managed lagoons or landfills, due to their high solubilities. Release to the atmosphere is also probable due to the high volatility of these compounds; volatilization poses the risk of direct inhalation of these toxic organic chemicals.
- 3) An appreciable amount of the waste is produced (calculated to be 720 metric tons in 1973). Approximately 75% of the total generated is paraldehyde.

## II. INDUSTRY AND PROCESS DESCRIPTION

### A. Profile of the Industry

Methyl ethyl pyridine (MEP) is a cyclic intermediate produced commercially by synthesis. Only limited information is available from which to draw an industry profile. A 1976 study<sup>(1)</sup> indicated that the 1973 U.S. production capacity was about 18,000 metric tons (40 million pounds). A more recent statistical review of the cyclic intermediates industry<sup>(2)</sup> does not include methyl ethyl pyridine among the cyclic intermediates for which production and sales data are available.

The TRW study <sup>(1)</sup> identified Union Carbide as a major producer of 2-methyl-5-ethyl pyridine (Diagram I, below). This appears to be the isomer of major commercial importance.<sup>(1,3)</sup> Koppers Company, Inc., Nepara Chemical Company, Inc., and Reilly Tar and Chemical were cited as other producers. Chem Sources-USA, 1980 edition<sup>(4)</sup> lists RIT-Chem Company, Inc. as a producer of 4-methyl-3-ethyl pyridine.



No important commercial end uses of MEP have been identified.<sup>(3,5)</sup> 2-Methyl-5-ethyl pyridine is a raw material used for the industrial production of nicotinic acid (3-pyridien-3-carboxylic acid) by

nitric acid oxidation and decarboxylation.(3) It is also a precursor for 2-methyl-5-vinyl pyridine (MVP), which is used in acrylic fiber manufacture and in some styrene/butadiene polymer formulations. Producers of MEP end products identified in Chem Sources-USA(4) are Vitamins, Inc. (nicotinic acid) and Philips Chemical Company (methyl vinyl pyridine).

#### B. Manufacturing Process

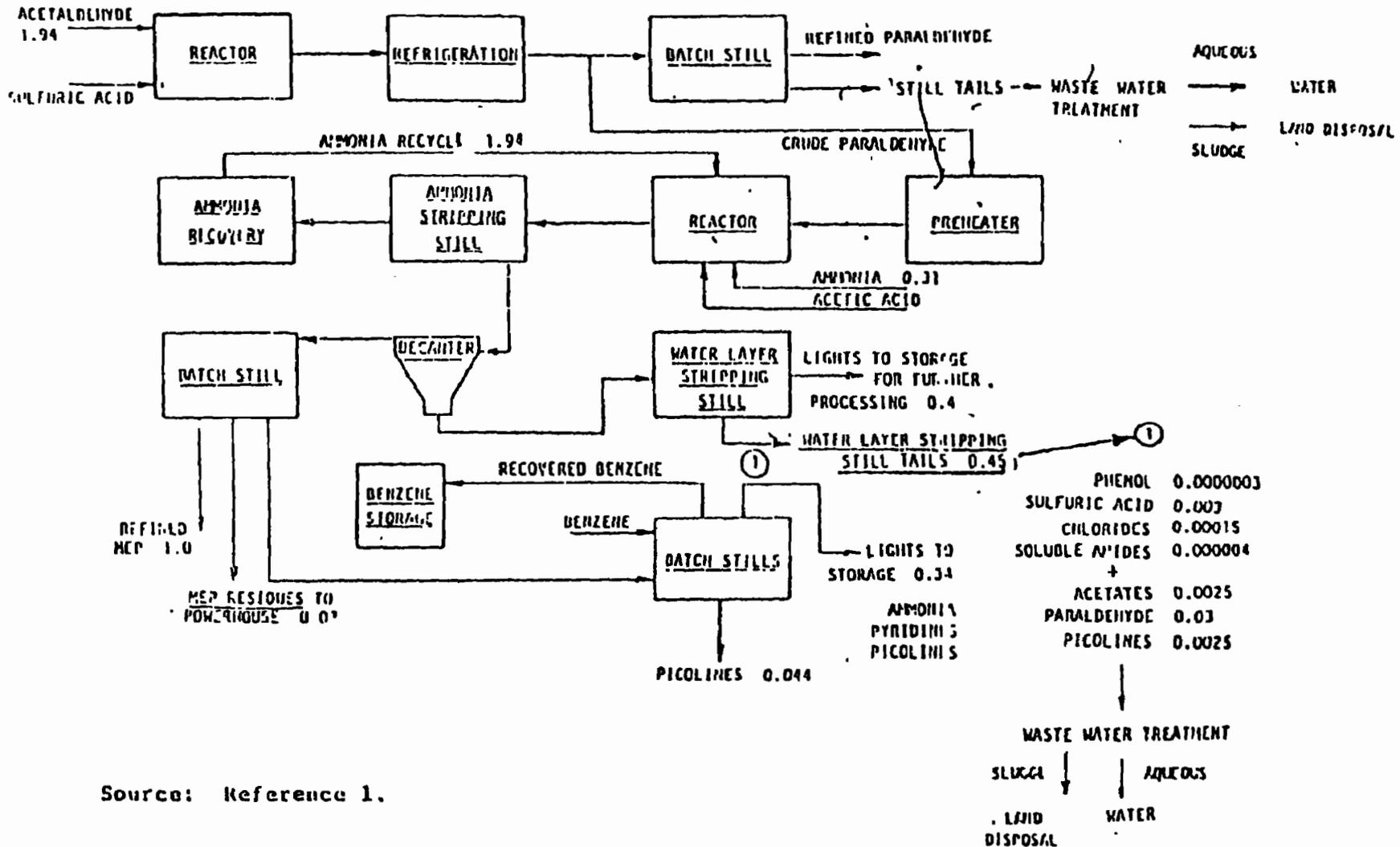
Methyl ethyl pyridine is among the pyridine bases that are produced commercially by synthesis (1,3,5), rather than by isolation from coal tar.

Figure 1 is the process diagram for MEP production. In the initial steps of MEP production, paraldehyde is usually generated at the plant site by reacting acetaldehyde with sulfuric acid to produce crude paraldehyde. A portion of the crude paraldehyde is used in the production of MEP, while the remaining portion is used for the production of refined paraldehyde. The batch still tails from paraldehyde production are sent to a wastewater treatment sytem.\*

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\*This waste stream is sent, along with the listed waste stream, to a lagoon. At this time, data is not available on the constituents in this waste stream. However, since the waste stream is mixed with the listed waste stream, the resulting mixture is defined by the Agency as being a hazardous waste, unless generators demonstrate otherwise.

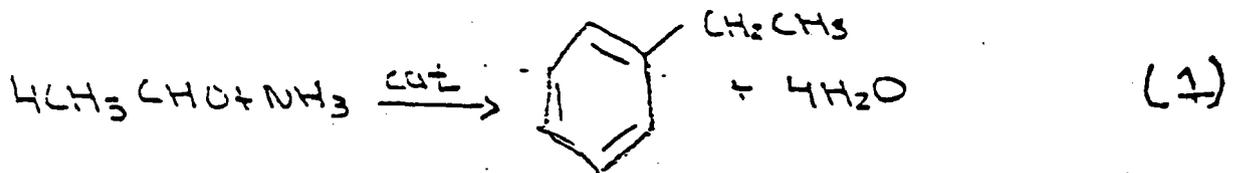
BASIS: 1 KG METHYL-ETHYL PYRIDINE



Source: Reference 1.

Figure 1: Pyridines (2-Methyl, 5-Ethyl Pyridine and α-Picoline) Manufacture.

After the production of the crude paraldehyde, 2-methyl-5-ethyl pyridine is synthesized in high yield from the liquid phase reaction of paraldehyde and ammonia acetate, aluminum oxide, ammonium fluoride or cobalt chloride catalyst.<sup>(3)</sup> This process which takes place in the reactor is shown by equation (1).<sup>(1)</sup>



As shown in the equation, an identified by-product in the reaction is 2-methyl pyridine (ϵ -picoline). The resulting process fluid is then transferred to an ammonia stripping still for ammonia recovery. The remaining fraction goes to a cleaner (decanter). The cleaned MEP fraction residue is further refined by a batch still.\* The residue from the cleaner is processed by a water layer stripping still. The stripping still tails from this process are labelled (1) in Figure 1.

### III. WASTE GENERATION AND MANAGEMENT

The stripping still tails are generated at a rate of approximately 0.04 Kg/Kg of refined MFP.<sup>(1)</sup> This amounts

\*The process effluent stream indicated as "MEP residues" from the batch still is not included in the waste listing because data is not yet available on the constituents in this waste stream.

to 720 metric tons of waste in 1973.

The TRW Study<sup>(1)</sup> identifies the following as the major contaminants in the listed waste stream:

paraldehyde	0.03 Kg/Kg MEP
sulfuric acid	0.003 Kg/Kg MEP
pyridines and picolines	0.0025 Kg/Kg MEP
soluble acetates	0.0025 Kg/Kg MEP
phenol	0.0000003 Kg/Kg MEP*

This data indicates that approximately 75 percent of the total waste accounted for is paraldehyde.

According to the 1976 study, industry practice is to manage the process effluent waste stream by sending it to wastewater treatment. As part of the wastewater treatment system, the waste is most likely stored/treated in lagoons.

#### IV. HAZARDOUS PROPERTIES OF THE WASTE

The waste is considered to pose a potential hazard to human health or the environment because of the presence of toxic organics.

All of these waste constituents are acutely or chronically toxic, and paraldehyde is included in the NIOSH list of suspect carcinogens (see pp. 11-16 for further health

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\*Phenol, while a hazardous waste constituent, is not deemed to be present in sufficient concentration to be of regulatory concern.

effects). The waste constituents are present in the wastes in high concentrations (see p. 6), and are also generated in fairly substantial quantities annually, so that there is a greater possibility of the hazardous constituents reaching environmental receptors should improper management occur. Exposure should also take place over longer periods of time, since substantial quantities of pollutants are available for environmental loading. Thus, the Agency would require some assurance that waste components will not migrate and persist to warrant a decision not to list this waste stream. No such assurance appears possible.

Each of the identified waste constituents has extremely high water solubility (indeed, pyridene and 2-picoline are infinitely water-soluble). (See Table 1.)

As a result of this high constituent solubility, this waste is likely to leach harmful constituents even under relatively mild environmental conditions, and to be highly mobile in ground and surface waters\* (App. B). If these wastes are exposed to more acidic environments, such as environments subject to acidic rainfall, the potential for waste migration increases. (See Table 1.)

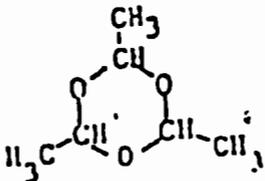
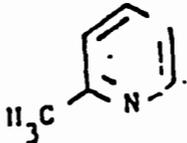
Current waste management practices involve wastewater treatment in lagoons. The potential for environmental

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\*Mobility through soil is expected to be high in light of these waste constituents' high solubilities. Further, disposal could occur in areas with permeable soils, so that mobility of waste constituents would not be substantially affected.

Table 1

Physical/Chemical Properties of Organics Identified  
in Stripping Still Tails<sup>a</sup>

Compound:	paraldehyde	pyridine	2-picoline <sup>b</sup>
Structure:			
Formula:	C <sub>6</sub> H <sub>12</sub> O <sub>3</sub>	C <sub>5</sub> H <sub>5</sub> N	C <sub>6</sub> H <sub>7</sub> N
NW:	132	79	93
B.P., °C:	128	115	129(143)
Vp, mm, 25°C:	10	22	10
Sat'd. vapor <sup>d</sup> conc'n, 25°C, g/m <sup>3</sup> :	71	93	50
Water solubility <sup>e</sup> :	v	inf.	v (inf.)
Octanol/water <sup>f</sup> partition co- efficient:	2.8(est.)	4.5	13
Acid dissociation constant <sup>g</sup> :		5.2	5.9 (5.7; 6.0)

<sup>a</sup> Except as noted, data are from Weast, Ref. 6

<sup>b</sup> Most data are available for 2-picoline. This is also the identified by-product of MEP production and therefore the isomer most likely present in the waste. Values in parentheses are for 3- and 4-picoline which have the same B.P. solubility

<sup>c</sup> Calculated from data in Weast(6) pD-123.

<sup>d</sup> Calculated from vapor pressure data:  $\text{g/m}^3 \frac{\text{VP}}{760} \times \frac{\text{MW}}{\text{RT}}$

Table 1 (Continued)

**e** v = very soluble (probably > 1%)

inf = infinitely soluble

s = soluble (probably > 0.1%)

**f** Source, Reference 7.

**g** For pyridine and picoline, value indicated is pka of the conjugate acid. Source, References 8,9.

contamination exists from improper lagooning, or through subsequent improper disposal of wastewater treatment sludges. Thus, improperly designed or managed lagoons - for example, those located in areas with permeable soils, or those lacking leachate control features -- could fail to prevent leachate migration into the environment in light of the solubility of the waste constituents, and the large amounts of available percolating liquid in the lagoon. Exposure via a surface water pathway is also possible if lagoons are constructed without proper flood control or wash out measures

If waste sludges are improperly landfilled they present a similar potential hazard. Lack of leachate control or improper siting thus could lead to waste migration.

Another pathway of concern is through airborne exposure to these volatile organics present in the stripping still tails. Some physical/chemical properties of the organic species that are relevant to their potential for adverse environmental impact are indicated in Table 1. Each of the organic species listed is highly volatile, with vapor pressures corresponding to saturation concentrations in the range of grams per cubic meter at 25°C (1 ppm (v/v) corresponds to about 1 milligram per cubic meter). Pyridine and 2-picoline are particularly volatile. Substantial fractions of contaminants present in the waste could thus volatilize to the atmosphere from lagoons and landfills that are not properly designed and operated, increasing the risk of inhalation of waste contaminants.

Once released from the matrix of the waste these constituents can persist and reach environmental receptors. Available data (21) indicates that biodegradation is the chief degradation mechanism with respect of paraldehyde and pyridine. Thus, these constituents could persist in the abiotic conditions of an aquifer similarly, persistence in air may occur.

#### V. HEALTH AND ENVIRONMENTAL EFFECTS

There is substantial evidence concerning the toxic effects of the organic species of concern. Table 2 summarizes some data from the Registry of Toxic Effects of Chemical Substances.<sup>(11)</sup> Paraldehyde is included in the NIOSH List of Suspected Carcinogens.<sup>(12)</sup>

##### 1. Paraldehyde

Paraldehyde exhibits moderate toxicity when ingested and low toxicity when applied to the skin.<sup>(13)</sup> Signs and symptoms of paraldehyde poisoning are uncoordination and drowsiness, followed by sleep. With larger doses, the pupils will dilate and reflexes will be lost; comotosis will follow. The symptoms of chronic intoxication from this material are disturbances of digestion, continued thirst, general emaciation, muscular weakness and mental fatigue.<sup>(13)</sup> Sax also warns that paraldehyde is dangerous and should be kept away from heat and open flames, because when heated, it emits toxic flames.<sup>(13)</sup>

Table 2

Summary of Data on Toxicity of Organics  
Identified in Stripping Still Tails(11)

PARAMETER	Compound		
	Paraldehyde	Pyridine	2-Picoline
LD <sub>Lo</sub> , oral-human mg/kg	14	500	--
LD <sub>50</sub> , oral-rat mg/kg	1530	891	790
OSHA standard (TLV) ppm/(v/v)	--	5	--
Aquatic Toxicity 96 hr TLm, ppm(w/v)	--	100-1000	--

## 2. Pyridines

Pyridines exhibit moderate toxicity when introduced to the human through oral, dermal and inhalation routes.(13) Liver and kidney damage have been produced in animals and in man, after oral administration.(14) In smaller doses, conjunctivitis, dizziness, vomiting, diarrhea and jaundice may appear;(15) also tremors and atoxia (deffective control of muscles), irritation of the respiratory tract with asthemic breathing, paralysis of eye muscles, paralysis of vocal chords and paralysis of bladder have been reported.(15) Threshold limit values (TLV) have been established by a number of countries for the protection of employees. These values should not be exceeded for an 8-hour shift of a 40-hour week:

USSR:	1.5 ppm = 5 mg/cum
USA:	5 ppm = 15 mg/cum
BRD*:	5 ppm = 15 mg/cum
Sweden:	5 ppm = 15 mg/cum

In drinking water pyridene produces a faint odor at 0.0037 ppm and is a taste and odor problem at 0.8 ppm.(16) Adverse taste in fish (carp, rudd) is reported at 5 ppm.(16) Pyridine causes inhibition of cell multiplication algae

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\* Federal Republic of Germany

(*Microcystis aeruginosa*) and bacteria (*Pseudomonas putida*) at 28 and 340 ppm, respectively. Sax<sup>(13)</sup> reports a number of other hazards associated with pyridines: (1) fire hazard, that is dangerous when it is exposed to heat, flame or oxidizer; (2) explosive hazard, that is severe when it is in the form of a vapor and is exposed to flame or spark; and (3) disaster hazard, that is dangerous when heated to decomposition, the pyridine emits highly toxic fumes of cyanides.

An EPA report<sup>(20)</sup> suggests that, based on health criteria, the ambient level of pyridines in water should not exceed 207 mg/L. On an ecological basis, it should not exceed 5000 mg/L.

### 3. Picolines

Picolines as a class exhibit high toxicity via dermal route and moderate toxicity via oral and inhalation routes.<sup>(13)</sup>  $\delta$ -picolines,  $\alpha$ -picolines and  $\beta$ -picolines are dangerous when heated to decomposition because of the emission of toxic fumes of NO<sub>x</sub>. The USSR has established a threshold limit value at 5 mg/m<sup>3</sup> for mixed isomers.<sup>(16)</sup>

An EPA report<sup>(20)</sup> suggests that, based on a health criteria, the ambient levels of picolines in water should not exceed 316 mg/l.

## REFERENCES

1. U.S. EPA. Assessment of industrial hazardous waste practices: Organic chemical, pesticides and explosives industries. EPA No. SW-118C. pp. 5-26 to 5-28 NTIS PB No. 251 307. 1976.
2. United States International Trade Commission. Synthetic organic chemicals: United States production and sales. USITC Publication 1001. pp. 33-80. 1979.
3. Abramovitch, R. A. Pyridine and pyridine derivatives. In: E. P. Dukes, C. Coleman, P. Hirsch, G. Joyce, P. Van Reyden and G. C. Wronker, eds. Kirk-Othmer Encyclopedia of Chemical Technology. 2nd ed., V. 16. John Wiley and Sons, New York. pp. 780-803. 1968.
4. Baker, M. J., B. D. Bradley, C. L. Gandenberger, E. M. Giordano, J. B. Mertz, L. E. Nash and M. S. Nash, eds. Chem-Sources-USA, 1980 ed. Directories Publishing Co., Ormond Beach, Florida. pp. 296. 1980.
5. Astle, M. J. Industrial organic nitrogen compounds, ACS monograph series. Reinhold Publishing Corporation, New York. pp. 134-145. 1961.
6. West, R. C., ed.-in-chief. Handbook of chemistry and physics. 47th Ed. Chemical Rubber Company. Cleveland, Ohio. 1966.
7. Hansch, C., and A. J. Leo. Substituent constants or correlation analysis in chemistry and biology. John Wiley and Sons, New York. 1979.
8. Perrin, D. D. Dissociation constants of organic bases in aqueous solution. Butterworths, London. 1965.
9. Kortum, G., W. Vogel and K. Andrussov. Dissociation of organic acids in aqueous solution. Butterworths, London. 1961.
10. Not used in text.
11. Lewis, R. J., Sr., and R. L. Tatked, eds. NIOSH. Registry of toxic effects of chemical substances. U.S. Department of Health, Education and Welfare. 1978.

12. U.S. EPA. An ordering of the NIOSH suspected carcinogens list. EPA No. 660/1-76-003. NTIS PB No. 251 851. 1976.
13. Sax, N. I. Dangerous properties of industrial materials, 5th ed. Van Nostrand Reinhold Company, New York. 1979.
14. Deichmann, W. R. Toxicology of drugs and chemicals. Academic Press, Inc., New York. 1969.
15. The International Technical Information Institute. Toxic and Hazardous Industrial Chemical Safety Manual for Handling and Disposal with Toxicity and Hazard Data. Toranomon-Tachikawa Bldg., 6-5. 1 Chome, Nishi-Shimbashi, Minato-ku. Tokyo, Japan. 1976.
16. Verschueren, K. Handbook of environmental data on organic chemicals. Van Nostrand Reinhold Company, New York. 1977.
18. Not used in text.
19. Not used in text.
20. Cleveland, J. G., and G. L. Kingsbury. Multimedia environmental goals for environmental assessment, V. 2. EPA No. 600/7-77-136b. November, 1977.
21. Dawson, English and Petty. Physical chemical properties of hazardous waste constituents. 1980.

LISTING BACKGROUND DOCUMENT  
TOLUENE DIISOCYANATE PRODUCTION

Centrifuge and distillation residues from toluene diisocyanate production (R,T)\*

I. Summary of Basis for Listing

The centrifuge and distillation residues from the production of toluene diisocyanate (TDI)\*\* contain toxic organic substances, mutagenic substances, and substances that are probably carcinogenic. The wastes are also highly reactive upon contact with water. These wastes result from the production of toluene diisocyanate through the coupling of toluene diamines and phosgene.

The Administrator has determined that toluene diisocyanate wastes may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- 1) The TDI centrifuge and vacuum distillation wastes consist of toluene diisocyanates which are toxic and toluene diamines which are suspected carcinogens.
- 2) More than 6000 metric tons of TDI production wastes are produced per year.
- 3) Storage in drums in a landfill, a past management method for this waste, poses a risk because toluene diisocyanate (TDI) is a highly reactive, pressure-generating compound which has caused explosion of drums. Several such damage

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\*This listing description has been clarified, in response to comments, to indicate that wastes from both centrifuge and distillation processes are included.

\*\*This compound is also referred to as tolylene diisocyanate or tolyl diisocyanate.

incidents have occurred demonstrating the potential for improper disposal of diisocyanate wastes.

- 4) In addition to the reactivity hazard, this waste could leach toxic toluene diamine into groundwater, if improperly managed, posing a human health risk.

## II. Sources of the Waste and Typical Disposal Practices

### A. Profile of the Industry

Toluene diisocyanate (TDI) production in the United States in 1973<sup>(1)</sup> was 330,000 metric tons (661 million pounds). The major producers of mixed toluene diisocyanate isomers<sup>(1)</sup> in 1979 were Allied Chemical Corporation (Specialty Chemicals Division), BASF Wyandotte Corporation, E. I. duPont de Nemours and Company, Inc., Dow Chemical, U.S.A., Mobay Chemical Company, Olin Corporation, Rubicon Chemicals Inc., and Union Carbide Corporation. Toluene diisocyanate is the major intermediate for the production of polyurethanes. A typical TDI continuous process plant capacity is 27,500 metric tons (60 million pounds per year). The process is illustrated in Figure 1.

### B. Manufacturing Process (9,10)

The starting raw materials for a continuous process plant are a solution of toluene-2,4-diamine, 2,6-toluene-diamine, or an 80:20 mixture of the two, an inert solvent (o-dichlorobenzene) and gaseous phosgene. These compounds are fed to two jacketed, agitator-equipped reactor kettles, in series, along with recycled solvent where the

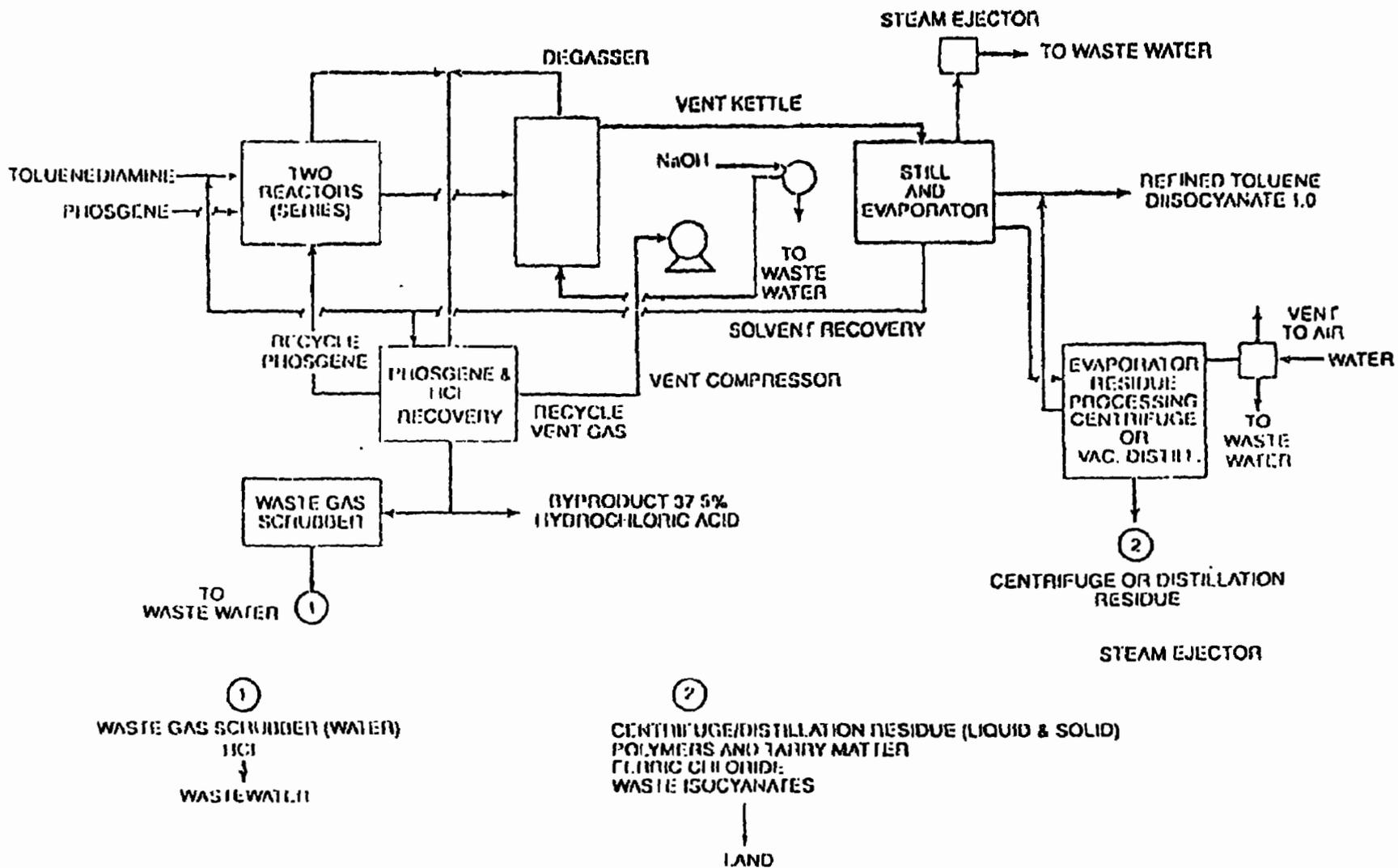


Figure 1. TOLUENE DIISOCYANATE MANUFACTURE  
(MODIFIED FROM REFERENCE 9)

following reactions shown in Figures 2 and 3 take place. An excess of phosgene is used in this process step. The unreacted phosgene and hydrogen chloride formed by the reaction constitute the major components of the gas stream exiting the second reactor. The reactor exit gas goes to a phosgene recovery/by-product hydrochloric acid recovery system. All equipment is vented to scrubbers. The phosgene and hydrogen chloride are recovered in the scrubbers.

The recovered phosgene is recycled as a solution in the recovered solvent to the first reactor. The by-product hydrochloric acid (2.32 Kg of 37.5 percent HCl/Kg TDI product) is recovered from the gas stream after removal of the phosgene and is stored or sold. The waste gas scrubber effluent, containing residual hydrogen chloride (0.025 Kg/Kg TDI product) dissolved in water, is neutralized and then sent to the plant industrial outfall.

The dehydrochlorination to form TDI takes place after the reactor liquid (from Reactor 2) has been fed to the degasser. The reaction products from the second reactor are dehydrochlorinated by blowing an inert gas such as natural gas through the solution to remove HCl. The degasser gas is then sent to the phosgene and HCl recovery system, where the HCl and phosgene are recovered as noted above and the inert gas is recycled.

The crude TDI solution from the degassers is fed to the stills and evaporators to recover o-dichlorobenzene solvent and purify the TDI. The purified TDI is sent to storage. The recovered solvent is recycled for use in recovery of phosgene and as a solvent for the toluenediamine

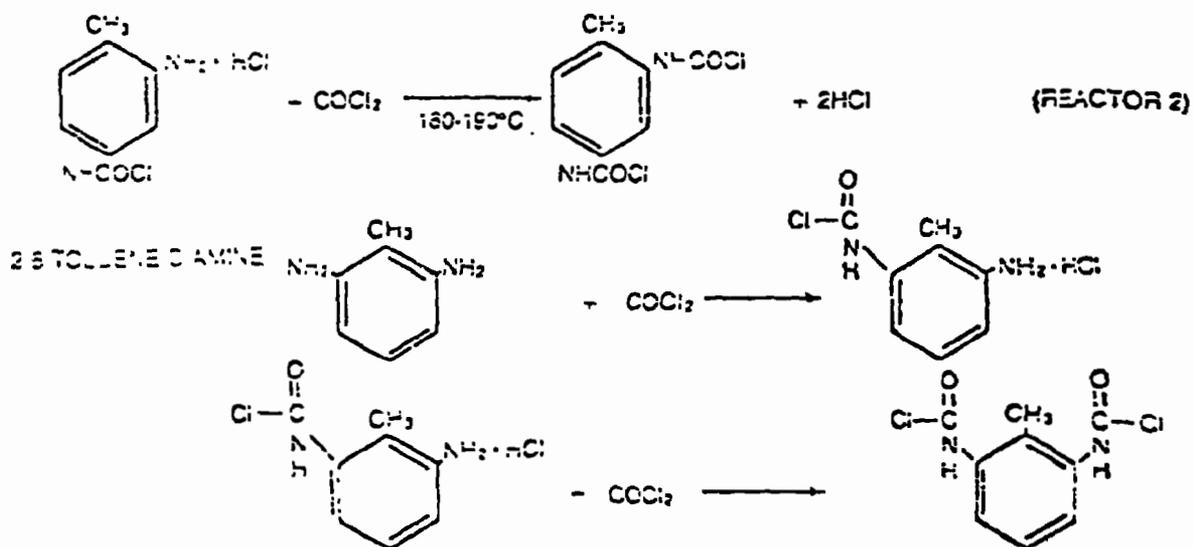
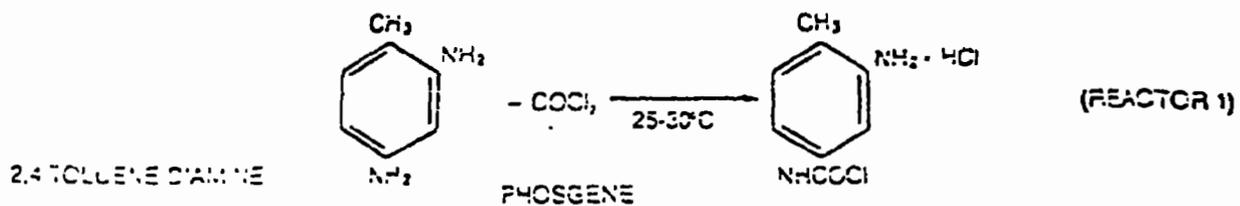


Figure 2. REACTIONS OF 2,4 AND 2,5-TOLUENEDIAMINE (9)

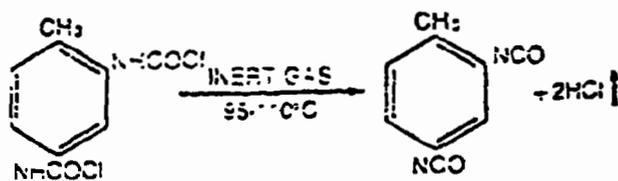


Figure 3. DEHYDROCHLORINATION REACTION TO FORM TDI (9)

feed. The liquid evaporator residue containing some TDI and waste products is then further processed by either centrifugation or vacuum distillation to recover additional TDI product. The remaining centrifugation or vacuum distillation residue is the waste stream listed in this document.

### C. Waste Generation and Management

Approximately 0.021 Kg of waste are generated per Kg of TDI produced.<sup>(11)</sup> Based on 1973 production, this results in an excess of 6000 metric tons of centrifuge and distillation residues requiring disposal. The material contains 90 percent polymers and tarlike matter, 6 percent ferric chloride (largely from process impurities) and 3 percent waste isocyanates.<sup>(11)</sup>

The wastes have been known to be disposed of in both on- and off-site landfills, and on occasion to be containerized in drums prior to landfilling. (See pp. 437-438 following.) Current industry practice, however, as determined through a poll of its member companies by the International Isocyanate Institute, Inc. indicates that storage of residues in drums in landfills is not a known management method.<sup>(14)</sup>

### III. Discussion of Basis for Listing

#### A. Hazards Posed by the Waste

As shown above, the 6000 metric tons of TDI production wastes that are generated annually are expected to contain the following components:

- o Polymers and tarlike materials - 90%
- o Ferric chloride - 6%
- o Waste isocyanates (including TDI) - 3%

The waste isocyanates are toxic and the free isocyanates are potentially highly reactive with other materials, including water.

#### 1. Reactivity Hazard

Toluene diisocyanate, and other free isocyanates present in TDI waste, are known to react violently upon contact with water. The reaction of free isocyanate groups with water usually occurs very rapidly, is exothermic, and results in the violent formation of aromatic diamines and carbon dioxide gas. The disposal of these residues is potentially hazardous to the people handling them, since, should water come in contact with the waste, there could be explosive release of toxic and potentially carcinogenic aromatic chemicals over a wide area. A similar danger exists even if the wastes are drummed, since if water enters, dangerously high pressures can result in rupture of the drum, followed by explosive release of the contaminants. For this reason, long-term storage of these wastes in steel drums at waste disposal sites is considered extremely hazardous if containment is breached and water infiltrates the drum.

There have been several damage incidents associated with improper disposal of toluene diisocyanate wastes, which confirm that this waste stream is reactive. In California in 1978, a drum containing TDI waste was picked up by a scavenger waste hauler and placed in an unprotected storage area. After having been exposed to rain, the drum was then removed

to a Class I landfill where it exploded, requiring the hospitalization of several people.\* In Detroit in May of 1978, a tank truck waiting to dispose of a quantity of TDI waste experienced a boil-over. As a result nine people exposed to the toxic fumes were hospitalized.\*

These damage incidents illustrate the hazards created by improper treatment, storage or disposal of TDI production waste. In view of the above information, it is apparent that the waste meets the standard for reactivity set in §261.23(a) (2) and (4).

## 2. Toxicity Hazard Via Ground and Surface Water Exposure Pathways

These wastes also pose a hazard via ground and surface water pathways due to their toxicity and potential for genetic harm. The principal component of concern for this route of exposure is toluene-2,4-diamine, which is produced by the reaction of diisocyanates with water, and is a suspect carcinogen.\*\* (See pp. 8-10 following.)

This substance is capable of migrating from improperly designed and managed waste disposal sites. Toluene-2,4-diamine, produced by the reaction of the diisocyanates with water (12), is very soluble (13).

Thus, if waste disposal sites are designed improperly or are improperly managed--for example sited in areas with highly permeable

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\*OSW Hazardous Waste Division, Hazardous Waste Incidents, unpublished, open file, 1978.

\*\*Toluene diisocyanate, while toxic, is too reactive to persist in water, and so probably would not pose a toxicity hazard via water. It may, however, pose a toxicity hazard in direct handling of the waste.

soils, or constructed without natural or artificial liners--there is a possibility of escape of waste constituents to groundwater. A further possibility of substantial hazard arises during transport of these wastes to off-site disposal facilities. This increases the likelihood of their being mismanaged, and may result either in their not being properly handled during transport or in their not reaching their destination at all, thus making them available to do harm elsewhere. A transport manifest system combined with designated standards for the management of these wastes will thus greatly reduce their availability to do harm to human beings and the environment. The damage incidents described above in fact demonstrate hazards which may arise during off-site transportation and management.

The Agency presently lacks reliable data as to the environmental persistence of the waste constituents of concern. It is assumed however, that waste constituents are persistent enough to remain in the environment long enough to cause substantial hazard, a conclusion supported by the actual damage incidents involving these wastes.

A final reason for listing these wastes as hazardous is the quantity of wastes generated. The wastes are generated in fairly substantial quantity--6,000 MT annually. Thus, large quantities of hazardous constituents are available for environmental release, increasing the likelihood of exposure if the wastes are mismanaged. Large expanses of groundwater could similarly be polluted. Contaminant migration also may occur for long periods of time, since large amounts of pollutants

are available for environmental loading. All of these considerations increase the possibility of exposure, and support a hazardous waste listing.

B. Health and Ecological Effects

1. Toluene Diisocyanate

Health Effects - TDI is toxic [inhalation rat LD<sub>50</sub>=600ppm/6hr.] and is an irritating material, both in its liquid and airborne forms, because of its high reactivity. It can produce skin and respiratory tract irritation, and can cause sensitization so that sensitized individuals are subject to asthmatic attacks upon re-exposure to extremely low concentrations of TDI. Additional information and specific references on the adverse effects of TDI can be found in Appendix A.

Regulations - The OSHA standard for toluene diisocyanate is 5 ppb, with a ceiling of 20 ppb in 10 minutes.

Industrial Recognition of Hazard - Sax's Dangerous Properties of Industrial Materials<sup>(2)</sup> designates toluene diisocyanate as an emitter of highly toxic fumes containing hydrogen cyanide when heated to decomposition.

2. Toluene-2,4-diamine

Health Effects - Toluene-2,4-diamine is a suspect carcinogen<sup>(3)</sup>. Although it did not cause cancer in animals upon skin painting,<sup>(4)</sup> it increased the incidence of lung cancer in the test animals. Toluene diamine was also shown to induce liver tumors<sup>(5)</sup> in rats,<sup>(6)</sup> morphological

aberrations in mammalian cells<sup>(7)</sup>, and causes bacterial mutation in the Ames test.<sup>(8)</sup> Additional information and specific references on the adverse effects of toluene 2,4-diamine can be found in Appendix A.

Industrial Recognition of Hazard - Toluene-2,4-diamine is designated in Dangerous Properties of Industrial Materials (Sax)<sup>(2)</sup> as moderately toxic when inhaled.

#### IV. References

1. U.S. Tariff Commission (U.S. International Trade Commission) Synthetic Organic Chemicals, United States Production and Sales. 1974 Preliminary Reports. Washington, U.S. Government Printing Office.
2. Sax, N. Irving. Dangerous Properties of Industrial Materials, Fourth Edition, Van Nostrand Reinhold Co., New York, 1975.
3. USEPA. Report 1980 Contract # 68-02-2773. Potential Atmospheric Carcinogens. Phase I - Identification and Classification, pp. 204.
4. Giles, A.L., et al. Dermal Carcinogenicity Study by Mouse-Skin Painting with 2,4-Toluenediamine Alone or in Representative Hair Dye Formulations. *J. Toxicol. Environ. Health*, 1(3):433-440, 1976.
5. Bridges, B.A., and M.H. Green. Carcinogenicity of Hair Dyes by Skin Painting in Mice (letter to editor). *J. Toxicol. Environ. Health*, 2(1):251-252, 1976.
6. Shah, M.J., et al. Comparative Studies of Bacterial Mutation and Hamster Cell Transformation Induced by 2,4-Toluenediamine (Meeting Abstract). *Proc. Am. Assoc. Cancer Res.*, 18:22, 1977.
7. *Cancer Research*, 29:1137, 1969.
8. Pienta, R.J., et al. Correlation of Bacterial Mutagenicity and Hamster Cell Transformations with Tumorigenicity Induced by 2,4-Toluenediamine. *Cancer Lett. (Amsterdam)*, 3(1/2): 45-52, 1977.
9. Lowenheim and Moran. Faith, Keyes, and Clark's Industrial Chemicals, 4th ed., John Wiley and Sons, 1975.
10. Kirk-Othmer. *Encyclopedia of Chemical Technology*. 3rd ed., John Wiley and Sons, Inc., New York, 1979.
11. Industrial Process Profiles for Environmental Use: Chapter 6, The Industrial Organic Chemicals Industry. Reimond Liepins, Forest Nixon, Charles Hudals, and Terry Parsons, February 1977, EPA-600/2-77-023f.
12. "Criteria for a Recommended Standard Occupational Exposure to TDI," U.S. Dept. of HEW, Public Health Service and National Institute of Occupational Safety and Health, HSM 73-110-22 (1973).
13. *Handbook of Chemistry and Physics*, 56th ed., Cleveland, CRC Press (1975).
14. Telephone communications between Rebecca Fields of EPA and Mr. Lee Hughes of the Mobay Chemical Corp., August 11, 1980.
15. Health and Environmental Effects Profile, Appendix A, 2,4-Toluenediamine, No. 161, April 30, 1980.

Response to Comments - Centrifuge Residue from Toluene Diisocyanate Production

Several comments were received with respect to waste K027 (Centrifuge residue from toluene diisocyanate production).

1. One commenter requested a clarification on the scope of waste listing K027. The commenter pointed out that the listing background document included both centrifuge and distillation residues as hazardous wastes, while the regulations specified only centrifuge residues. Therefore, the commenter felt it was unclear as to whether the Agency intended to limit the scope of the listed material to only wastes generated via a centrifuge unit operation.

In reviewing both the waste listing description as cited in the hazardous waste regulations (45 FR 33123) and the listing background document on toluene diisocyanate production, the Agency agrees that clarification is needed on the scope of waste listing K027. The Agency believes, however, it is quite clear from the listing background document that the listing was meant to include residues from both the centrifuge and distillation column since the composition/hazardousness of the waste when using either the centrifuge or distillation unit will not differ significantly (see listing background document TDI production: pg. 3, Figure 1 and pg. 6, 1st paragraph). This latter point was confirmed by Mr. Lee Hughes of the Mobay Chemical Corp., who explained that wastes from both a centrifuge and distillation column are comparable and that the type of waste generated depends on the type of

equipment used at the particular plant.<sup>(14)</sup> The final-final listing description, therefore, will be amended to include wastes generated from both the centrifuge and distillation column in the production of toluene diisocyanate.

2. The commenter also requested clarification as to whether the listing "centrifuge residue from toluene diisocyanate production" is limited to the undeactivated material as it is directly discharged from the distillation or centrifuge unit or whether it also would apply to de-activated material that results from any treatment of the waste (viz., the commenter indicated that each TDI producer de-activates TDI residues differently i.e., by wet quenching or aging, after generation of the final distillation or centrifuge bottoms).

The listing of waste from TDI production is limited to those undeactivated residues which are directly discharged from the centrifuge or distillation unit operation. Any deactivation of these residues would be considered a treatment process and would require a permit. Any producer which believes the treatment of these residues would render the waste non-hazardous non-reactive (i.e., no longer meeting the characteristic of reactivity) should submit a de-listing petition under §§260.20 and 260.22. It should be noted, however, that to de-list successfully residues which are generated from the centrifuge or distillation unit from the hazardous waste system, a generator must demonstrate that the waste is both non-reactive and non-toxic.

3. The listing "Centrifuge residue from toluene diisocyanate production" is listed as hazardous because it contains a number of toxic constituents, including toluene diisocyanate, toluene-2,4-diamine and tars (benzimidazapone). A number of commenters objected to the inclusion of these compounds as constituents of concern in this particular listing or had specific questions with respect to these toxic constituents.

More specifically:

-Toluene-2,4-diamine- The commenter indicates, that this compound is either not present in the waste or, if present, is only there in low concentrations (i.e., low ppm concentrations). Mr. Lee Hughes of the Mobay Chemical Co. indicated in conversation that most waste streams would not contain toluene-2,4-diamine since, among other things, it is not economical for the producer to waste the starting material. Additionally, the commenter indicated that analytical techniques used to conduct this determination are subject to variability.

-Toluene diisocyanate - The commenter indicates, that this compound is not a suspect carcinogen; the commenter also asserts that recent study results show that TDI is not carcinogenic and not mutagenic (it should be noted that the commenter did not provide any data or reference to any specific tests to support its claim).

- Tars (benzimidazapene) - the commenter indicated that although benzimidazapene is cited as the principal component in these tars, the commenter is not aware of the existence of this substance or any data to substantiate the claim that it is mutagenic or carcinogenic.

Therefore, the commenters recommend that all three of these toxic constituents be deleted as a basis for listing this waste.

The Agency disagrees with the commenter's first two points. Toluene-2,4-diamine has produced carcinogenic effects in rats and mice in a long-term feeding study (i.e., a suspect carcinogen) and was found to be mutagenic.<sup>(15)</sup> Additionally, it was found to be hepatotoxic to rats and mice and also hastened the development of chronic renal disease and accelerated animal morbidity.<sup>(15)</sup> Therefore, toluene-2,4-diamine is considered very toxic by the Agency, even at minimal levels. This is particularly true where the waste constituent is a suspect or proven carcinogen. As the Agency has stated, "There is no scientific basis for estimating 'safe' levels of carcinogens. The draft criteria for carcinogens therefore state that the recommended concentration for maximum protection of human health is zero"\*.

Consequently, even if toluene-2,4-diamine is present at low concentrations (low ppm) as claimed by the industry, the waste may well present a substantial hazard to human health and the environment should this waste constituent migrate and reach a receptor.

With respect to the commenter's concern on the variability of the analytical technique for toluene-2,4-diamine, the Agency has provided an analytical procedure for analyzing toluene-2,4-diamine (45 FR 33131: Appendix III, Table 1), and we will (necessarily) accept results obtained from use of this method. If an equivalent

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\*EPA Water Quality Criteria, 44 FR 15926, 15930 (March 15, 1979)).

or superior method is developed by the industry, a petition for equivalent testing or analytical methods can be submitted under §§260.20 and 260.21.

Toluene diisocyanate, while not a proven carcinogen (although it is still being evaluated), is nevertheless sufficiently toxic to present a substantial present or potential hazard to human health and the environment should it migrate from the waste (i.e., toluene diisocyanate exposure produces respiratory sensitization, decreased lung function, and exposure to high concentrations can result in pulmonary edema or death). Additionally, the reaction of free isocyanate groups with water usually occurs very rapidly, is exothermic, and results in a possible explosive release of toxic and potentially carcinogenic aromatic chemicals. In talking with Mr. Lee Hughes of the Mobay Chemical Corp.,<sup>(14)</sup> he indicated that toluene diisocyanate although present in the waste, is generally encapsulated or otherwise not available for human exposure, however, no data was submitted to support their contention. Therefore, the Agency believes that toluene diisocyanate is of regulatory concern, especially in light of past damage incidents, and will continue to include it as a constituent of concern in this particular listing. However, the Agency, will delete all reference to toluene diisocyanate as being a suspect carcinogen in the background document until a more definitive determination is made.

The listing of this waste stream for the presence of tars and the existence of "benzimidazapene" cannot be confirmed. Additionally, background information on chemical tars does not exist at this

time. Tars (benzimidazapene) therefore, will be removed as a constituent of concern in this particular listing.

4. Finally, one commenter argued that disposition of raw centrifuge residue in drums in a landfill is generally not practiced as a "known management method for this waste." This point was confirmed by the International Isocyanate Institute through a poll of its member companies (see ex parte communication from Rebecca Fields with Mr. Lee Hughes of the Mobay Chemical Co., August 11th, 1980.) Therefore, the commenter believes that the background document needs to be amended to reflect this information.

While disposal of these residues in drums in a landfill may not reflect current industry practice, the fact that past damage has occurred from this disposal method is evidence that improper management of these wastes in a probable mismanagement scenario may present a substantial present or potential hazard to human health and the environment (i.e., if these wastes are not controlled as hazardous, centrifuge residues may be sent to a sanitary landfill with no controls). Therefore, the Agency will continue to cite disposal of these residues in drums in a landfill as a possible mismanagement scenario. However, the Agency will amend the listing background document to indicate that disposal of these centrifuge residues in drums in a landfill is not a current disposal option, but has been practiced in the past.

## LISTING BACKGROUND DOCUMENT

### TRICHLOROETHANE PRODUCTION

- ° Waste from the product steam stripper in the production of 1,1,1-trichloroethane (T)
- ° Spent catalyst from the hydrochlorinator reactor in the production of 1,1,1-trichloroethane via the vinyl chloride process (T)
- ° Distillation bottoms from the production of 1,1,1-trichloroethane (T)
- ° Heavy ends from the production of 1,1,1-trichloroethane (T)

#### I. Summary of Basis for Listing

Waste from the heavy ends column, distillation column, and product steam stripper, and spent catalyst from the hydrochlorinator reactor in the production of 1,1,1-trichloroethane contain carcinogenic, mutagenic, teratogenic or toxic organic substances. The waste stream constituents of concern are 1,2-dichloroethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, and 1,1,2,2-tetrachloroethane, vinyl chloride, vinylidene chloride, and (possibly) chloroform.

The Administrator has determined that these solid wastes from 1,1,1-trichloroethane production may pose a substantial hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- 1) These wastes are listed as hazardous because they are likely to

contain 1,2-dichloroethane; 1,1,1-trichloroethane; 1,1,2-trichloroethane; 1,1,1,2-tetrachloroethane; 1,1,2,2-tetrachloroethane; vinylidene chloride; vinyl chloride and chloroform. Of these substances, 1,2-dichloroethane, 1,1,2-trichloroethane, vinylidene chloride, vinyl chloride and chloroform are recognized carcinogens and 1,1,1-trichloroethane is a suspected carcinogen; also a number of these chemicals have been found to be mutagenic in laboratory studies; the chlorinated ethanes also pass the placental barrier and several have been documented to produce teratogenic effects.

- 2) Significant quantities of wastes containing these hazardous compounds may be generated each year, increasing the possibility of exposure should mismanagement occur.
- 3) Mismanagement of incineration operations could result in the release of hazardous vapors to the atmosphere and present a significant opportunity for exposure of humans, wildlife and vegetation in the vicinity of these operations to potentially harmful substances through direct contact and also through pollution of surface waters. Disposal of these wastes in improperly designed or operated landfills could create a substantial hazard due to the potential of waste constituents to migrate and persist in aqueous environments.
- 4) Damage incidents illustrating the mobility and persistence of chloroethanes have occurred which resulted in surface and groundwater contamination.

## II. Sources of the Waste and Typical Disposal Practices

### A. Profile of the Industry

Currently, there are three producers of 1,1,1-trichloroethane in the United States. Table 1 lists the producers, sites, and estimated capacities of each plant. Actual production of this compound in 1978 was 644,475,000 pounds<sup>(3)</sup>.

The production of 1,1,1-trichloroethane has shown a steady increase in production as shown in Table 2. It is mainly used (92%) for metal degreasing and for electrical, electronic and instrument cleaning. Growth in the use of 1,1,1-trichloroethane is being accelerated because of the potentially greater health hazard exhibited by trichloroethylene.

TABLE 1

**1,1,1-Trichloroethane Producers, Sites, Capacities and Processes (1.2)**

<b>Company</b>	<b>Location</b>	<b>Annual Capacity (Millions of Pounds)</b>	<b>Process</b>
<b>Dow Chemical U.S.A.</b>	<b>Freeport, TX Plaquemine, LA</b>	<b>450 300</b>	<b>Via Vinyl Chloride</b>
<b>PPG Indus- tries</b>	<b>Lake Charles, LA</b>	<b>350</b>	<b>Via Vinyl Chloride</b>
<b>Vulcan Materials</b>	<b>Geismar, LA</b>	<b>65</b>	<b>Via Chloro- nation of ethane</b>
<b>TOTAL</b>		<b>1,165</b>	

TABLE 2

U.S. International Trade Commission  
1,1,1,-Trichloroethane Production (3)

Year	(Millions of Pounds)
1968	299.4
1969	324.3
1970	366.3
1971	374.6
1972	440.7
1973	548.4
1974	590.8
1975	
1976	631.2
1977	634.8

Other solvent uses are in formulating a variety of products including adhesives, spot cleaners and printing inks.

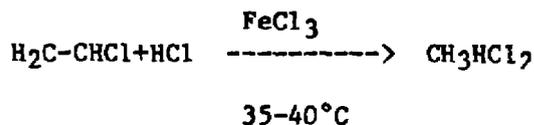
B. Manufacturing and Waste Generation Process\*

The bulk of 1,1,1-trichloroethane production in the United States is based upon the vinyl chloride process; minor amounts (-- 10%) are made by the ethane process. In the vinyl chloride process, vinyl chloride reacts with hydrogen chloride to form 1,1-dichloroethane, which is then thermally chlorinated to produce 1,1,1-trichloroethane. The yields based on vinyl chloride are approximately 95%.

1,1,1-Trichloroethane is also produced by the noncatalytic chlorination of ethane. Ethyl chloride, vinyl chloride, vinylidene chloride, and 1,1-dichloroethane are produced as co-products. When 1,1,1-trichloroethane is the only desired product, vinyl chloride and vinylidene chloride are hydrochlorinated to 1,1-dichloroethane and 1,1,1-trichloroethane respectively; ethyl chloride and 1,1-dichloroethane are recycled to the chlorination step (Kahn and Hughes, Monsanto Research Corp., Source Assessment: Chlorinated Hydrocarbons Manufacture, EPA 600/2-78-004, 1978).

Vinyl Chloride Process

The chemical reaction for the hydrochlorination of vinyl chloride is:



\*Based on the process description in Key, J.A. and Standifer, R.L., Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry," U.S. Environmental Protection Agency, EPA 68-02-2577, July 1979

Chlorination of 1,1-dichloroethane is represented as:

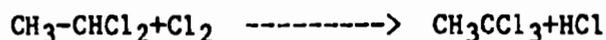


Figure 1 represents a simplified process for production of 1,1,1-trichloroethane via the vinyl chloride process. Vinyl chloride and hydrogen chloride\* (and the recycled overhead stream from the light ends column) react at 35-40°C in the presence of ferric chloride. The reactor effluent is neutralized with ammonia. The resulting solid complex (residual ammonium chloride, ferric chloride, and ammonia) is removed by the spent catalyst filter as a semisolid waste stream (Stream G, Fig. 1). The filtered hydrocarbon stream is then distilled in the heavy ends column and high-boiling chlorinated hydrocarbons (tars) are removed as a waste stream (Stream H, Fig. 1). The overhead from this column is further fractionated in the light ends column into two streams: 1,1-dichloroethane and the lighter components (primarily unreacted vinyl chloride). The lighter components are recycled to the hydrochlorination reactor. The 1,1-dichloroethane product is removed as the bottom stream and is then reacted with chlorine in the chlorination reactor at a temperature of about 400°C. The products from this reaction are distilled, and hydrogen chloride

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\*The hydrogen chloride (HCl) used for vinyl chloride hydrochlorination is often a by-product from the chlorination of 1,2 dichloroethane or from other processes in the plant complex. If by-product HCl is used, it can contain as much as 3.5% of 1,2-trichloroethane which will carry forward to the product stream stripper waste streams.

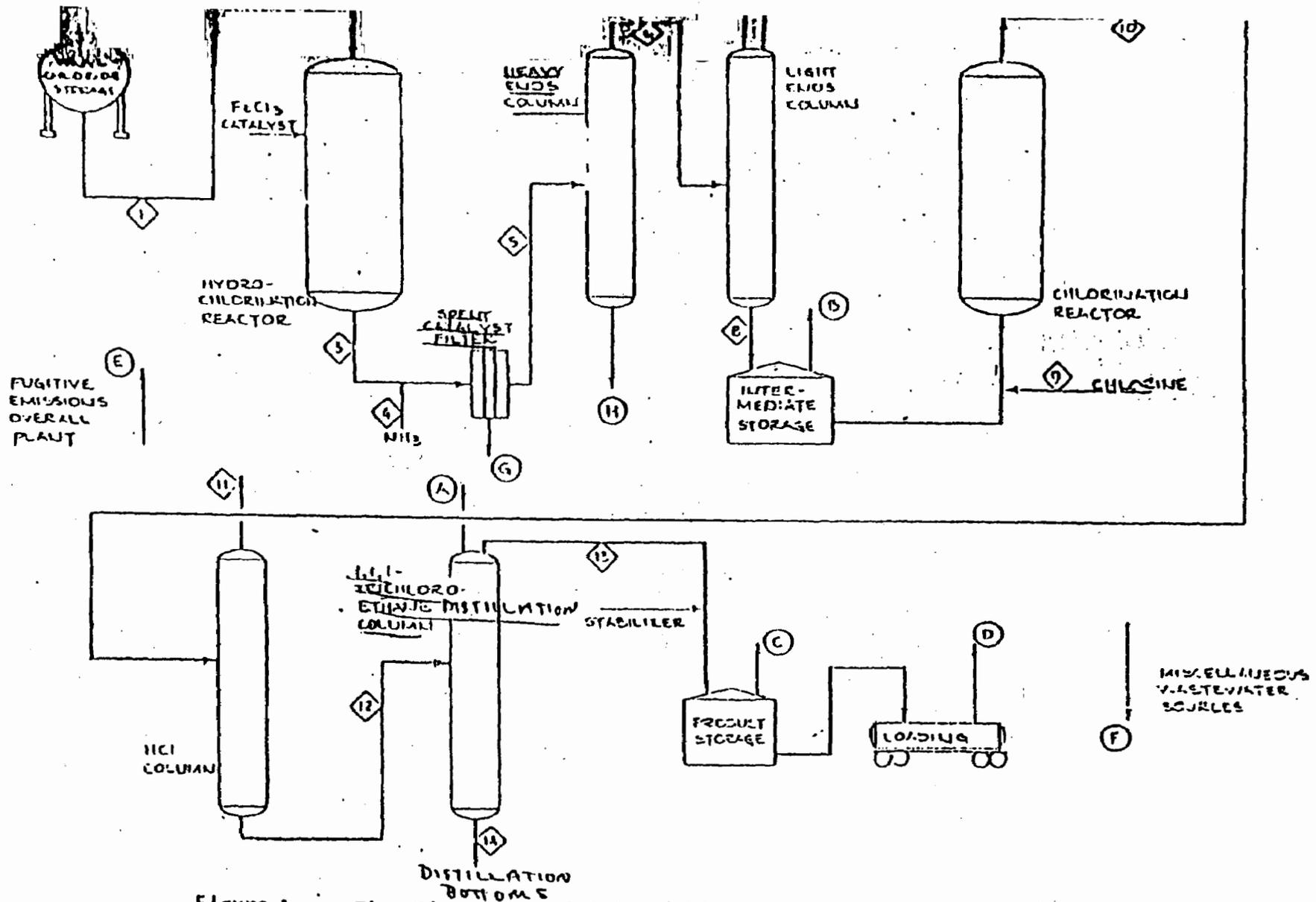


Figure 1. Flow Diagram for 1,1,1-Trichloroethane From Vinyl Chloride

-957-  
-475-  
-54-

and low boiling organic hydrocarbons are taken overhead in the HCl column. (This stream may be recycled to supply the hydrogen chloride required in the hydrochlorination step, or used for other chlorinated organic processes directly (e.g., oxy-chlorination processes)). The bottom stream from the hydrogen chloride column is further fractionated to recover 1,1,1-trichloroethane as the overhead product, which, after the addition of a stabilizer, is stored. The bottom stream from the 1,1,1-trichloroethane column is comprised largely of 1,1,2-trichloroethane, tetrachloroethanes, and pentachloroethanes (stream 14, Fig. 1). (These bottoms may be used as a feedstock for production of other chlorinated hydrocarbons (e.g., perchloroethylene-trichloroethylene, vinylidene chloride), in which case they will not be discarded.) Estimated emissions from this process are shown in Table 3. The listed waste streams are shown in Figure 1 as follows: spent catalyst wastes are noted as stream G, heavy ends as stream H, and distillation bottoms as stream 14.

Certain 1,1,1-trichloroethane production processes use a steam stripper prior to final distillation and recovery of 1,1,1 trichloroethane, in which case a separate waste stream is generated. The attached Figure 2 shows a process where a steam stripper is used.

#### Chlorination of Ethane

The main sequence of reactions occurring during the free radical chlorination of ethane is:



TABLE 3

## ESTIMATED EMISSIONS FROM 1,1,1-TRICHLOROETHANE MANUFACTURE: Vinyl Chloride Process

Species	EMISSIONS kg/Mg		
	Air	Aqueous	Solid
Hydrogen chloride	1.6		
Ethane	1.6		
Ethene			
NH <sub>4</sub> -FeCl <sub>3</sub> -3 Complex			2.2
1,1-Dichloroethane	2.2		
1,1-Dichloroethene	9.9		0.8
1,2-Dichloroethane			0.8
1,1,1-Trichloroethane	3.5		3.9
1,1,2-Trichloroethane	2.6		51.2
1,1,1,2-Tetrachloroethane			35.3
1,1,2,2-Tetrachloroethane			40.8
Pentachloroethane			1.8
Sodium hydroxide		33.7	
Sodium chloride		449.	

Source: Elkin, L.M. "Chlorinated Solvents," Process Economic Program Report No. 48, Stanford Research Institute, Menlo Park, California, February, 1969.

Small amounts of 1,2-dichloroethane and 1,1,2-trichloroethane are also formed in minor amounts. The product mix, however, can be varied somewhat by operating conditions. Furthermore, to maximize 1,1,1-trichloroethane production, ethyl chloride and 1,1-dichloroethane are recycled to the chlorination reactor; vinyl chloride and vinylidene chloride are catalytically hydrochlorinated to 1,1-dichloroethane and 1,1,1-trichloroethane respectively:

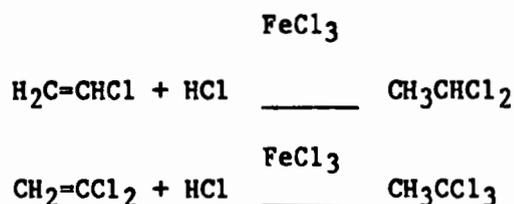


Figure 3 represents a simplified process for production of 1,1,1-trichloroethane via direct chlorination of ethane. Chlorine and ethane react in an adiabatic reactor at an approximate temperature of 400°C and a pressure of 6 atmospheres with a residence time of approximately 15 seconds. The reactor effluent (containing unreacted ethane, ethylene together with vinyl chloride, ethyl chloride, vinylidene chloride, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,1-trichloroethane, a small amount of higher chlorinated hydrocarbons, and hydrogen chloride) is quenched and cooled. The bottom stream from the quench column, consisting primarily of tetrachloroethane and hexachloroethane, is removed. The overhead product from the quench column is fractionated into a chlorinated hydrocarbon stream and light products -- ethane, ethylene, and hydrogen chloride. A portion of the crude hydrogen chloride stream is used in subsequent hydrochlorination reactions; excess hydrogen chloride is purified for reuse or resale. The bottom stream from

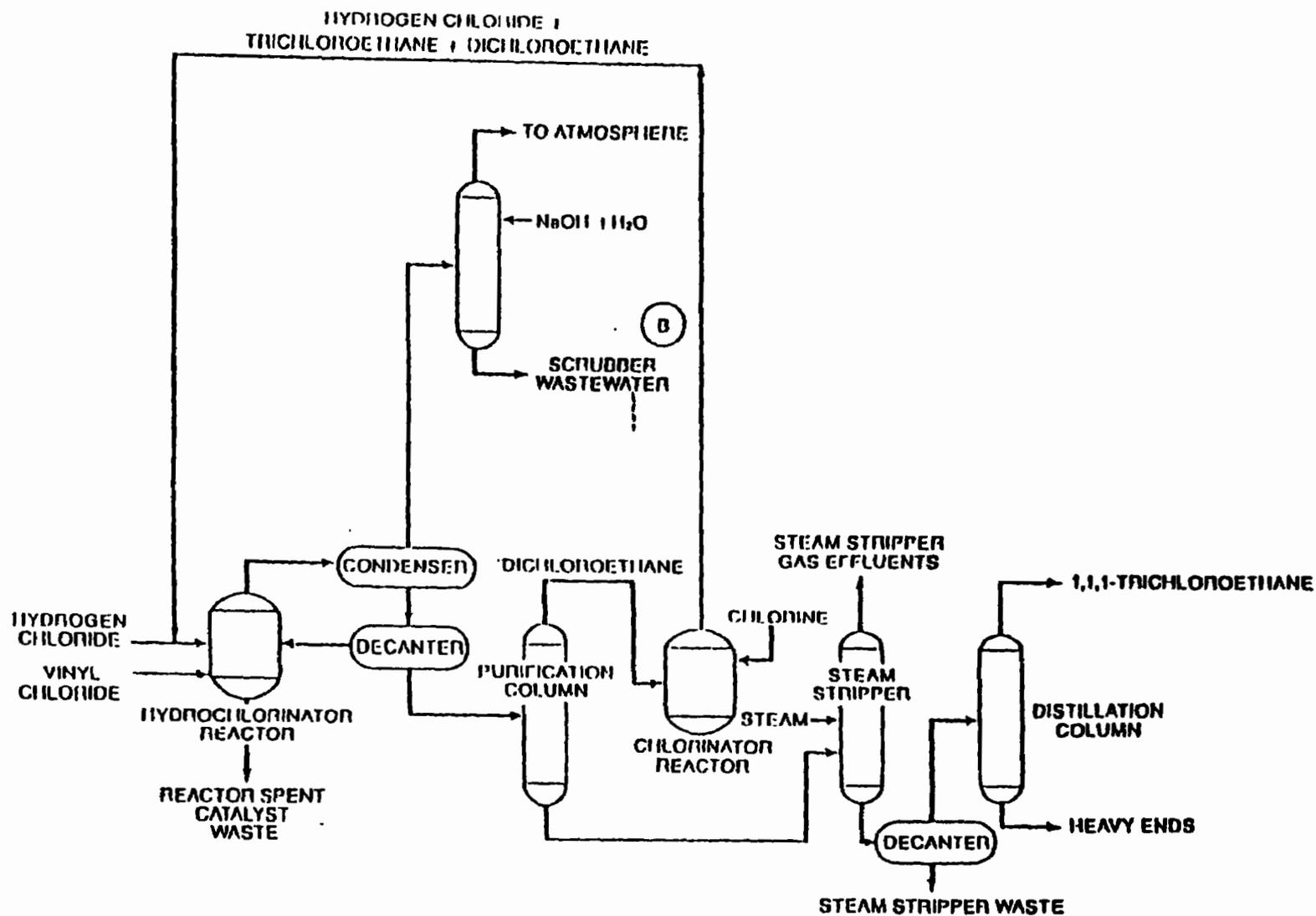


Figure 2. 1,1,1-TRICHLOROETHANE BY THE HYDROCHLORINATION AND DIRECT CHLORINATION OF VINYL CHLORIDE. (51)



the hydrogen chloride column is further separated by distillation into various products. The lower boiling hydrocarbons are removed as an overhead product in the first column. The bottoms contain substantially all the heavy waste materials (tetrachlorinated ethanes and higher). The bottoms may be disposed of as waste or used in other chlorinated hydrocarbon processes as a feedstock. These bottoms are the waste stream of concern from the ethane chlorination process. (The remaining process description is provided for informational purposes.)]

The overhead product (principally 1,1,1-trichloroethane, vinyl chloride, vinylidene chloride, ethyl chloride, and 1,1-dichloroethane) is fractionated and 1,1,1-trichloroethane removed as a bottom product. The overhead stream from the 1,1,1-trichloroethane column is fed to the 1,1-dichloroethane column, where 1,1-dichloroethane is separated as the bottoms stream and is recycled as a feedstock to the chlorination reactor. Vinyl chloride, vinylidene chloride, and ethyl chloride (the overhead stream) are fed to the hydrochlorination reactor, where vinyl chloride and vinylidene chloride react with hydrogen chloride to form 1,1-dichloroethane and 1,1,1-trichloroethane respectively. Approximate hydrochlorination reaction conditions are at a temperature of 65°C and 4 atm.

The reactor effluent stream from the hydrochlorination reactor is neutralized with ammonia. The resulting complex (ammonium chloride-ferric chloride - ammonia) is removed by the spent catalyst filter as a semisolid waste. (This is the analogous stream to the spent catalyst waste in the vinyl chloride process (see Fig. 1), but is not

listed as hazardous when arising in the ethane chlorination process since it consists principally of iron chloride and hydrogen chloride (see Table 4)). The filtered hydrocarbon stream is fractionated further: the bottom fraction (primarily 1,1,1-trichloroethane) is recycled to the trichloroethane column. The overhead stream (primarily ethyl chloride and 1,1-dichloroethane) is recycled to the chlorination reactor. Table 4 summarizes the estimated emissions from this process. As shown, predicted waste constituents are 1,2-dichloroethane, 1,1,1-trichloroethane and higher boiling ethanes which are expected to comprise the major percentage of the waste.

Table 5 summarizes waste constituents and estimated waste constituent amounts in waste streams generated by each process.

#### C. Waste Management Practices

The Agency presently lacks reliable information as to the management practices for these wastes, but based on typical waste management practices in the chlorinated organic manufacturing industry it is likely that distillation bottoms and heavy ends are landfilled (perhaps in drums). Aqueous wastes are probably stored on site in pits that equalize surges in the waste flow to landfill operations. Some wastes also may be incinerated.

### III. Discussion of Basis for Listing

#### A. Hazards Posed by the Waste

The various waste streams from the production of 1,1,1-trichloroethane are likely to be generated in large quantities, as indicated by a comparison of the waste emission factors contained in Tables 3, 4, and 5 and the production data in Table 2. Such substantial

TABLE 4

ESTIMATED EMISSIONS FROM 1,1,1-TRICHLOROETHANE MANUFACTURE: Chlorination of Ethane

Species	<u>Air</u>	EMISSIONS kg/Mg	
		<u>Aqueous</u>	<u>Solid</u>
Ethene	2.4		
1,1-Dichloroethane			trace
1,2-Dichloroethane			30.7
1,1,1-Trichloroethane			39.0
1,1,2-Trichloroethane			49.7
Tetrachloroethanes			
Hexachloroethanes			51.4
Iron (III) chloride			
Hydrogen Chloride			<u>2.8</u>
			<u>173.6</u>

Source: Elkin, 1969

TABLE 5

Via Vinyl Chloride Process

<u>Waste Stream</u>	<u>Compound</u>	<u>kg/Mg of 1,1,1-Trichloroethane</u>
Distillation bottoms and heavy ends	1,1,2-trichloroethane	51.2
	1,1,1,2-tetrachloroethane	35.3
	1,1,2,2-tetrachloroethane	40.8
	Pentachloroethane	1.8
Waste from product stream stripper*	1,2-dichloroethane	0.8
	1,1,1-trichloroethane*	3.9*
Spent catalyst**	NH <sub>4</sub> Cl-FeCl <sub>3</sub> -NH <sub>3</sub> complex**	2.2**

Via Chlorination of Ethane

<u>Waste Stream</u>	<u>Compound</u>	<u>kg/Mg of 1,1,1-trichloroethane</u>
Heavy ends	1,1-dichloroethane	trace
	1,2-dichloroethane	30.7
	1,1,1-trichloroethane	49.7
	1,1,2-trichloroethane	49.7
	tetrachloroethanes) hexachloroethanes )	51.4

\*The spent steam stripper waste is also expected to contain small concentrations of vinyl chloride, vinylidene chloride and chloroform. Vinyl chloride is expected to be present since it is a feedstock constituent. Vinylidene chloride is a by-product from the dehydrochlorination of 1,1,2-trichloroethane. Chloroform is another predicted reaction by-product, and is expected to be formed from the splitting off of vinyl chloride monomer and ethane into single carbons, which are subsequently chlorinated.

\*\*The spent catalyst waste is also expected to contain small concentrations of vinyl chloride feedstock, 1,1,1-trichloroethane product and some polymeric materials.

waste quantities are themselves of regulatory concern in light of the hazardous constituents present. Thus, waste mismanagement poses the threat of contaminating large expanses of groundwater, surface water and air, and of reaching large numbers of environmental receptors.

Of the chemicals potentially present in the wastes, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,1,2,2-tetrachloroethane, vinylidene chloride, vinyl chloride and chloroform are on the CAG carcinogen list; 1,1,1-trichloroethane is a suspected carcinogen and 1,1,1-tetrachloroethane is toxic.\* Some of these chemicals are also suspected mutagens and teratogens. Should these compounds reach human receptors, the potential for resulting adverse health effects would be extremely high. These constituents are capable of migration. For example, 1,2 dichloroethane, the trichloroethanes, and the tetrachloroethanes all are relatively soluble in water (solubility ranging from 200 ppm - 8700 ppm) (App. B), and thus, these compounds are capable of causing chronic toxicity via a water exposure pathway. Indeed, if they solubilize these compounds could pose a substantial hazard at a level many orders of magnitude less than their solubility limits. In addition, 1,2-dichloroethane and 1,1,2-trichloroethane are fairly volatile as well (vapor pressure 60 mm Hg.)\*\*; thus, 1,1,2-trichloroethane and the tetrachloroethanes may pose a chronic toxicity

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\*Pentachloroethane poses some threat of chronic exposure via an inhalation pathway, but is not presently considered to pose sufficient danger to be listed as a waste constituent of concern.

\*\*1,1,1 trichloroethane is also volatile, but is expected to photolyse rapidly so probably would not pose a substantial hazard via air inhalation beyond the immediate disposal site (App. B.).

problem via inhalation as well.<sup>(47)</sup>

These waste constituents are capable of mobility and persistence as well, as shown by numerous damage incidents involving these waste constituents. Chlorinated ethane and ethylene contamination of groundwater in areas adjacent to disposal sites in fact is not uncommon. For example, 1,1,1-trichloroethane has been detected in groundwater in Acton, MA, where residents believe the source is a disposal site at a nearby manufacturing facility.<sup>(4)</sup> In New Jersey, seepage from landfilled wastes near the CPS Chemical Company also resulted in well contamination by trichloroethylene, tetrachloroethane, and methylene chloride<sup>(5)</sup>. 1,2-dichloroethane has also been detected in groundwater supplies in Bedford, MA, where the source of contamination has not been positively identified but is believed to be due to industrial uses upstream.<sup>(4)</sup> Dichloroethanes are among the waste constituents which have migrated from Hooker Chemical's facility at Montague, Mich., contaminating large expanses of ground and surface water.<sup>(48)</sup> Trichloroethane has also migrated and contaminated private drinking wells in Canton, Connecticut.<sup>(4A)</sup>

Thus, these wastes are capable of causing substantial hazard unless properly managed, and the possibility of mismanagement and environmental release of contaminants is certainly plausible. Some portion of these wastes are expected to be landfilled, while other residues are expected to be incinerated. Improper landfilling — siting in areas with permeable soils, inadequate leachate control or monitoring, lack of landfill cover, and the like -- could allow waste constituents to leach into groundwater, or escape via volatilization.

Even if plastic lined drums are used for disposal, they represent a potential hazard if the landfill is improperly designed or operated (i.e., drums corrode in the presence of even small amounts of water). The current disposal sites (the Gulf Coast) receive considerable rainfall and have a high ground water table creating a potential for drum corrosion.

Given the presence of the chlorinated ethanes and ethylenes and the potential for drum degradation, it is likely that these wastes, if improperly landfilled (i.e., improperly designed or operated landfill), would come into contact with ground water. This is particularly true of deeper deposits or those in cooler climates where vapor losses will be minimized. In these two cases, the waste constituents will readily move with the groundwater, just as they have been observed to do at sites such as Love Canal, the Kin-Buc Landfill, and Story Chemical in Michigan County, Michigan.(49,50,51,52) The above damage incidents support laboratory findings that any released 1,1,2-trichloroethane and 1,2-dichloroethane will pass through sandy soils with less than a 50 percent loss due to volatilization(6).

In addition to landfilling, the 1,1,1-trichloroethane steam stripper bottoms which are recycled or incinerated is often stored temporarily at the production site. Should leaks occur, similar problems to those from landfills could be expected.

Mismanagement of incinerating operations could result in the release of hazardous vapors, containing among other substances the waste constituents of concern, to the atmosphere and present a signifi-

cant opportunity for exposure of humans, wildlife and vegetation in the vicinity of these operations to potentially harmful substances through direct contact and also through pollution of surface waters.

Finally, should these waste constituents migrate into the environment they can be expected to persist, thus increasing the likelihood of reaching environmental receptors and causing substantial harm. The damage incidents above demonstrate environmental persistence of the released constituents. All of these waste constituents are expected, on the basis of literature degradation values, to persist in groundwater. (1,1,2-Trichloroethane is subject to hydrolysis, but has a hydrolysis half-life of 6 months. 1,1,2-Trichloroethane may also persist in air as well (App. B)). Again, the persistence of these constituents is evidenced by the measurable concentrations of these chemicals in Love Canal leachate some thirty years after disposal.(49.50.51) In any case, in light of the hazardous character of these waste constituents, the Agency could not justify a decision not to list these wastes absent assurance that waste constituents are incapable of migration and persistence. As demonstrated above, such assurance is not possible.

#### B. Health and Ecological Effects

##### 1. 1,2-Dichloroethane

Health Effects - 1,2-Dichloroethane is a carcinogen;(7) it has also been identified by the Agency as demonstrating substantial evidence of carcinogenicity.(54) In addition, this compound and several of its metabolites are highly mutagenic (8,9). 1,2-Dichloroethane crosses the placental barrier and is embryotoxic and teratogenic(10-14), and has been shown to concentrate in the milk of

nursing mothers.(15) Exposure to this compound can cause a variety of adverse health effects including damage to the liver, kidneys and other organs, internal hemorrhaging and blood clots(16). 1,2-Dichloroethane is designated a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse health effects of 1,2-dichloroethane can be found in Appendix A.

Ecological Effects - Values for a 96-hour static  $LC_{50}$  for bluegills ranged from 236 to 300 mg/l.(17)

Regulations - OSHA has set the TWA at 50 ppm. DOT requires the containers for this chemical to carry a warning that it is a flammable liquid.

The Office of Air, Radiation and Noise has completed pre-regulatory assessment of 1,2-dichloroethane under Sections 111 and 112 of the Clean Air Act. Pre-regulatory assessments are also being conducted by EPA's Office of Water and Waste Management under the Safe Drinking Water Act and by the Office of Toxic Substances under the Toxic Substances Control Act.

Industrial Recognition of Hazard - Sax, in Dangerous Properties of Industrial Materials, rates 1,2-dichloroethane as highly toxic upon ingestion and inhalation.

## 2. 1,1,1-Trichloroethane (Methyl Chloroform)

Health Effects - The area of greatest health concern regarding 1,1,1-trichloroethane exposure involves its potential for mutagenic, teratogenic and carcinogenic effects. In vitro studies have indicated that 1,1,1-trichloroethane is slightly mutagenic with

or without activation.(20,57,58) These studies were performed using the Ames system which is characterically insensitive to chlorinated hydrocarbons. 1,1,1-Trichloroethane was also positive in an in vitro mammalian cell transformation assay.(19) However, the results of two animal carcinogen bioassay studies were inconclusive due to design and experimental problems.(18,20,56) The NCI is currently re-evaluating the carcinogenic potential of 1,1,1-trichloroethane. Studies of the teratogenic potential of 1,1,1-trichloroethane are also suggestive; however, more studies are needed to make a conclusive statement.(56)

Other than psychophysiological effects, 1,1,1-trichloroethane exposure at or below the OSHA-PEL (350 ppm) does not result in either acute or chronic toxic complications. At very high concentrations (710,000 ppm), however, 1,1,1-trichloroethane produces cardiovascular and CNS narcotic effects, and can cause death from cardiac failure. Animal studies as well as accidental human exposure, have shown that, at these high inhalation concentrations, 1,1,1-trichloroethane produces a "chlorinated hydrocarbon" type of microscopic pathology liver and kidneys (fatty infiltration, cellular necrosis) which is characterized as being much less severe than that produced by carbon tetrachloride or trichloroethylene. Additional information and specific references on the adersion effects of 1,1,1-trichloroethane can be found in Appendix A.

Ecological Effects - Lethal concentrations (LC<sub>50</sub>, 96 hour values) are reported ranging from 33 mg/l (Dab), and 70 mg/l (Sheepshead minnow) to 69.7 mg/l (Bluegill) and 105 mg/l (Flathead

minnow).(24,56)

1,1,1-Trichloroethane in common with other volatile hydrocarbons, volatilizes from water to an appreciable extent. However, retransport to water from the atmosphere and decreased volatilization rates from stagnant water render the aquatic compartment an important sink for 1,1,1-trichloroethane. The major ecological concern, however, is its possible role as an ozone depleter. In recent years there has been considerable concern over human activities appreciably altering the levels of ozone in the stratosphere. The tropospheric lifetime of 1,1,1-trichloroethane is believed to be in the range of 4-12 years, and it has been estimated that 10-20 percent of the 1,1,1-trichloroethane molecules released at the earth's surface will eventually reach the stratosphere.(59) Studies simulating conditions obtained at high altitudes have shown(60) that the lax resident time of 1,1,1-trichloroethane in the stratosphere and the high solar uv intensity will result in its eventual total destruction yielding free Cl atoms which are known to destroy stratospheric ozone.

Regulations - 1,1,1-Trichloroethane is designated as a priority pollutant under Section 307(a) of the CWA. OSHA has set the TWA at 350 ppm. EPA has recommended an ambient water quality criterion at 15.7 mg/l. Because of wide use and exposure, and the inadequacy of currently available information, the TSCA Interagency Testing Committee has recommended(55) further evaluation to establish the carcinogenicity, mutagenicity and teratogenicity and other chronic effects of 1,1,1-trichloroethane.

Industrial Recognition of Hazard - Sax (Dangerous Properties of Industrial Materials) lists 1,1,1-trichloroethane as moderately toxic via inhalation.

### 3. 1,1,2-Trichloroethane

Health Effects - 1,1,2-Trichloroethane has been shown to cause cancer in mice; (25) it has also been identified by the Agency as demonstrating substantial evidence of carcinogenicity. (54) There is evidence that 1,1,2-trichloroethane is mutagenic and may be embryotoxic or cause teratogenic effects. (26,27)

Like the other compounds of this type, the trichloroethanes are narcotics that produce central nervous system effects, and can damage the liver, kidney and other organs. (15)

1,1,2-Trichloroethane is designated as a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of 1,1,2-trichloroethane can be found in Appendix A.

Ecological Effects - Aquatic toxicity data are limited with only three acute studies in freshwater fish and invertebrates, with doses ranging from 10,700 to 22,000 ug/l. (17)

Regulations - OSHA has set the TWA at 10 ppm (skin).

### 4. Vinylidene Chloride

Health Effects - Vinylidene chloride has been shown to cause cancer in laboratory animals (28,29) and to be mutagenic. (28) It has also been identified by the Agency as demonstrating substantial evidence of carcinogenicity. (54) It is very toxic [LD<sub>50</sub> (rat) = 200 mg/kg] and chronic exposure can cause damage to the

liver and other vital organs as well as causing central nervous system effects. Additional information and specific references on the adverse effects of vinylidene chloride can be found in Appendix A.

Regulations - DOT requires containers to be labeled "flammable liquid." OSHA has set the TWA at 10 ppm.

Industrial Recognition of Hazard - The toxic hazard of vinylidene chloride is suspected of being similar to vinyl chloride which is moderately toxic via inhalation (Sax, Dangerous Properties of Industrial Materials)(30).

#### 5. Vinyl Chloride

Health Effects - Vinyl chloride has been shown to be a carcinogen in laboratory studies;(31,32,33) it has also been identified by the Agency as demonstrating substantial evidence of carcinogenicity.(54) This finding has subsequently been supported by epidemiological findings.(33-37)

Vinyl chloride is very toxic [LD<sub>50</sub> (rat) = 500 mg/kg] and acute exposure results in anaesthetic effects as well as uncoordinated muscular activities of the extremities, cardiac arrhythmias(38) and sensitization of the myocardium.(39) In severe poisoning, the lungs are congested and liver and kidney damage also occur.(40) A decrease in white blood cells and an increase in red blood cells was also observed, as well as a decrease in blood clotting ability.(41) Vinyl chloride is designated as a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of vinyl chloride can be found in Appendix A.

Regulations - OSHA has set the TWA at 1 ppm with a 5 ppm ceiling over 15 minutes. DOT requires this to be labeled "flammable gas."

Industrial Recognition of Hazard - Vinyl chloride has a moderate toxic hazard rating via inhalation (Sax, Dangerous Properties of Industrial Materials).

#### 6. Chloroform

Health Effects - Chloroform has been shown to be carcinogenic(42,54) and tangential evidence links human cancer epidemiology with chloroform contamination of drinking water.(43,44) Chloroform has also been shown to induce fetal toxicity and skeletal malformation in rat embryos.(45,46) Chronic exposure causes liver and kidney damage and neurological disorders.(43) Additional information and specific references on the adverse effects of chloroform can be found in Appendix A.

Ecological Effects - The U.S. EPA has estimated that chloroform accumulates fourteen-fold in the edible portion of fish and shell fish.(43) The U.S. EPA has also recommended that contamination by chloroform not exceed 500 ug/l in freshwater and 620 ug/l in marine environments.(43)

Regulations - Chloroform has been designated as a priority pollutant under Section 307(a) of the CWA. OSHA has set the TWA at 2 ppm. FDA prohibits use of chloroform in drugs, cosmetics and food contact material. The Office of Water and Waste Management has proposed regulation of chloroform under Clean Water Act Section 311 and is in the process of developing regulations under Clean Water Act 304(a).

The Office of Air, Radiation and Noise is conducting preregulatory assessment of chloroform under the Clean Air Act. The Office of Toxic Substances has requested additional testing of chloroform under Section 4 of the Toxic Substances Control Act and is conducting pre-regulatory assessment under the Federal Insecticide, Fungicide and Rodenticide Act.

Industrial Recognition of Hazard - Chloroform has been given a moderate toxic hazard rating for oral and inhalation exposures (Sax, Dangerous Properties of Industrial Materials).<sup>(30)</sup>

#### 7. Tetrachloroethanes

Health Effects - 1,1,2,2-Tetrachloroethane has been shown to produce liver cancer in laboratory mice;<sup>(31)</sup> it has also been identified by the Agency as demonstrating substantial evidence of carcinogenicity.<sup>(54)</sup> It is also shown to be very toxic [oral rat LD<sub>50</sub> = 200 mg/Kg.]. In addition, passage of 1,1,1,2-tetrachloroethane across the placental barrier has been reported.<sup>(29)</sup> In Ames Salmonella bioassay 1,1,2,2-tetrachloroethane was shown to be mutagenic.<sup>(32)</sup> Occupational exposure of workers to 1,1,2,2-tetrachloroethane produced neurological damage, liver and kidney ailments, edema, and fatty degeneration of the heart muscle.<sup>(33)</sup> Both 1,1,1,2-tetrachloroethane and 1,1,2,2-tetrachloroethane are designated as priority pollutants under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of tetrachloroethanes can be found in Appendix A.

Ecological Effects - Freshwater invertebrates are sensitive to 1,1,2,2-tetrachloroethane with a lethal concentration of 7-8 mg/l being reported.<sup>(20)</sup> USEPA estimates the BCF to be 18.

Regulations - OSHA has set the TWA at 5 ppm (skin) for  
1,1,2,2-tetrachloroethane.

Industrial Recognition of Hazard - Sax, Dangerous  
Properties of Industrial Materials, lists 1,1,2,2-tetrachloroethane  
as being highly toxic via ingestion, inhalation and skin absorption.

#### IV. References

1. 1979 Director of Chemical Producers United States.
2. Chemical Economics Handbook, Menlo Park, California. December 1978. (May be purchased from SRI.)
3. Synthetic Organic Chemicals, U.S. Production and Sales, U.S. International Trade Commission.
4. Water Quality Issues in Massachusetts, Chemical Contamination, Special Legislative Commission on Water
5. Memo from Roy Albert to E. C. Beck, Administrator, EPA Region II, Drinking Water Contamination of New Jersey Well Water. March 31, 1978.
6. Wilson, J. T., and C. G. Enfield, 1979, Transport of Organic Pollutants Through Unsaturated Soil. Presented American Geophysical Union. December 3-7, San Francisco, CA.
7. National Cancer Institute. Bioassay of 1,2-Dichloroethane for Possible Carcinogenicity. U.S. Department of Health, Education and Welfare, Public Health Service, National Institutes of Health, National Cancer Institute, Carcinogenesis Testing Program, DHEW Publication No. (NIH) 78-1305, January 10, 1978.
8. McCann, J., E. Choi, E. Yaasaki, and B. Ames. Detection of Carcinogens as Mutagenic in the Salmonella/Microsome Test: Assay of 300 Chemicals. Proc. Nat. Acad. Sci. USA 72(2): 5135-5139, 1975a.
9. McCann, J., V. Simmon, D. Streitwieser, and B. Ames. Mutagenicity of Chloroacetaldehyde, a Possible Metabolic Product of 1,2-Dichloroethanes (ethylene dichloride), Chloroethanol (ethylene chlorhydrin), Vinyl chloride, and Cyclophosphamide. Proc. Nat. Acad. Sci. 72 (8):3190-3193.
10. Vozovaya, M., Changes in the Esterous Cycle of White Rats Chronically Exposed to the Combined Action of Gasoline and Dichloroethane Vapors. Akush. Genicol. (Kiev) 47 (12): 65-66, 1971.
11. Vozovaya, M., Development of Offspring of Two Generations Obtained from Femals Subjected to the Action of Dichloroethane. Gig. Sanit. 7:25-28, 1974.
12. Vozovaya, M., The Effect of Low Concentrations of Gasoline, Dichloroethane and Their Combination on the Generative Function of Animals and on the Development of Progeny. Gig. Tr. Prof. Zabol. 7:20-23, 1975.

13. Vozovaya, M., Effect of Low Concentrations of Gasoline, Dichloroethane and Their Combination on the Reproductive Function of Animals. Gig. Sanit. 6:100-102, 1976.
14. Vozovaya, M. A., The Effect of Dichloroethane on the Sexual Cycle and Embryogenesis of Experimental Animals. Akush. Genecol. (Moscos) 2:57-59, 1977.
15. Urusova, T. P. (About a possibility of dichloroethane absorption into milk of nursing women when contacted under industrial conditions.)
16. Parker, J. C., et al. 1979. Chloroethanes: A Review of Toxicity. Amer. Indus. Hyg. Assoc. J., 40: A 46-60, March 1979!
17. U.S. EPA, 1979. Chlorinated Ethanes: Ambient Water Quality Criteria (Draft).
18. NCI, 1977. Bioassay of 1,1,1-Trichloroethane for Possible Carcinogenicity. Carcinog. Tech. Rep. Ser. NCI-CG-TR-3.
19. Price, P. J., et al. 1978. Transforming Activities of Trichloroethane and Proposed Industrial Alternatives. In vitro. 14:290.
20. U.S. EPA Report, In Vitro Microbiological Mutagenicity of 81 Compounds.
21. Schwetz, B. A., et al. 1974. Embryo and Fetal Toxicity of Inhaled Carbon Tetrachloride and Dichloroethane and Methyl Chloroform in Rats. Toxicol. Appl. Pharmacol. 28:452.
22. Stahl, C. J., et al. 1969. Trichloroethane Poisoning. Observations on the Pathology and Toxicology of Six Fatal Cases. Jour. Forensic Sci., 14:393.
23. Walter P., Chlorinated Hydrocarbon Toxicity, a Monograph. PB-257185. National Technical Information Service, Springfield, Virginia.
24. U.S. EPA, 1979. In-Depth Studies on Health and Environmental Impact of Selected Water Pollutants. Contract No. 68-01-4646.
25. Chlorinated Solvents, Lloyd Elkin. February 1969. (May be purchased from SRI.)
26. Elovaara, E., et al. Effects of CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>Cl<sub>3</sub>, TCE, Perc and Toluene in the Development of Chick Embryos, Toxicology 12: 111-119, 1979.
27. Parker, J. C., I. W. F. Davidson and M. M. Greenberg, EPA Health Assessment Report of 1,2-Dichloroethane (Ethylene Dichloride). In preparation.

28. Environmental Health Perspectives, 1977, Vol. 21, 333 pp.
29. Van Duuren, B. L., et al. 1979. Carcinogenicity of Halogenated Olefinic and Aliphatic Hydrocarbons in Mic. J. Nat. Cancer Inst. 63(6): 1433-1439.
30. Sax, N. I. Dangerous Properties of Industrial Materials.
31. Viola, P. L., et al., Oncogenic Response of Rat Skin, Lungs, and Bones to Vinyl Chloride. Cancer Res. 31: 516, 1971.
32. Maltoni, C., and G. Lefemine, Carcinogenicity Bioassays of Vinyl Chloride. Am. NY Acad. Sci. 246: 195 (1975).
33. Lee, F. I., and Harry D. S., Angiosarcoma of the Liver in a Vinyl Chloride Worker. Lancet 1: 1316 (1974).
34. Creech & Johnson, Angiosarcoma of the Liver in the Manufacture of Polyvinyl Chloride. Jour. Occup. Med. 16: 150, 1974.
35. Falk, H., et al. Hepatic disease among workers at a Vinyl Chloride Polymerization Plant. Jour. Amer. Med. Assoc. 230: 59 (1974).
36. Makk, L., et al. Liver Damage and Liver Angiosarcoma in Vinyl Chloride Workers. Jour. Amer. Med. Assoc. 230: 64 (1974).
37. Tabershaw, I. R., and Gaffey, W. R., Mortality Study of Workers in the Manufacture of Vinyl Chloride and its Polymers. Jour. Occup. Med. 16: 509 (1974).
38. Oster, R. H., et al. Anesthesia, XXVII, Narcosis with Vinyl Chloride Anesthesiology 8: 359, 1947.
39. Carr, J., et al. Anesthesia XXIV. Chemical Constitution of Hydrocarbons and Cardiac Automaticity. J. Pharmacol. 97:1 (1949).
40. Torkerson, T. R., et al. The Toxicity of Vinyl Chloride by Repeated Exposure of Laboratory Animals - Amer. Ind. Hyg. Assoc. Jour. 22:354 1961.
41. Lester, D., et al. Effects of Single and Repeated Exposures of Humans and Rats to Vinyl Chloride. Amer. Ind. Hyg. Assoc. Jour. 24: 105, 1963.
42. National Cancer Institute, 1976. Report on Carcinogenesis Bioassay of Chloroform. National Technical Information Service, PB-245018. Springfield, Virginia.
43. U.S. EPA, 1979. Trichloromethane (Chloroform) Hazard Profile, USEPA-ECAO, Cincinnati, Ohio 45268. 1979.

44. McCabe, L. J., 1975. Association Between Trihalomethanes in Drinking Water (NORS Data) and Mortality. Draft Report. U.S. EPA.
45. Schwetz, B. A., et al. The effect of maternally inhaled trichloroethylene, perchloroethylene, methyl chloroform and methylene chloride on embryonal and fetal development in mice and rats. Toxicol. Appl. Pharmacol. 32: 84-96.
46. Thompson, D. J., et al. 1974. Teratology Studies on Orally Administered Chloroform in the Rat and Rabbit. Toxicol. Appl. Pharmacol. 29: 348.
47. Dawson, English, and Petty, 1980. "Physical Chemical Properties of Hazardous Waste Constituents", Table 1.
48. EPA, Hazardous Waste Division, Technology and Management Assessment Branch, "Animal Study of Personal Injury, Economic Damage or Fatalities from Hazardous Waste", 1978.
49. Barth, E. F., Cohen, J. M., "Evaluation of Treatability of Industrial Landfill Leachate", unpublished report, U.S. EPA, Cincinnati, November 30, 1978.
50. O'Brien, R. P., City of Niagara Falls, New York, Love Canal Project, unpublished report. Calgon Corp., Calgon Environmental Systems Division, Pittsburgh, Pennsylvania.
51. Rcera Research, Inc. Priority Pollutant Analyses prepared for Nuco Chemical Waste Systems, Inc., unpublished report, Tonawanda New York, April, 1979.
52. Sturino, E., Analytical Results: Samples From Story Chemicals, Data Set Others 336", unpublished data, U.S. EPA Region 5, Central Regional Laboratories, Chicago, Illinois, May, 1978.
53. Source Assessment Chlorinated Hydrocarbons Manufacture. EPA-600/2-78-004.
54. CAG List of Carcinogens, April 22, 1980.
55. U.S. EPA. Second Report of the TSA Interagency Testing Committee to the Administrator, EPA, OTS, April 1979.
56. 44 FR 34685-34692 (June , 1979).
57. Simmon, V. F., K. Kauchaven, and R. G. Tardiff. 1977. "Mutagenic activity of chemicals identified in drinking water" in: Progress in Genetic Toxicology, ed. I. D. Scott, B. A. Bridges and F. R. Sobels. pp. 249-258, Elsevier, N.Y.

58. McCann, J. and B. Ames, 1976. Detection of carcinogens as mutagens in the Salmonella microsome test: assay of 300 chemicals. Proc. Nat. Acad. Sci. 78: 950.
59. National Academy of Science, 1979. Stratospheric ozone depletion by halocarbons: chemistry and transport. NRC, NAS. Washington, D.C.
60. U.S. EPA. 1980. Final Report on Risk Assessment of 1,1,1-trichloroethane. Contract Number 68-01-0543. Batelle Columbus Laboratories, Columbus, Ohio 43201.

Response to Comments - Waste from the Product Steam Stripper  
and Spent Catalyst from the Hydrochlorinator Reactor in the Production  
of 1,1,1-Trichloroethane

One commenter raised several questions with respect to wastes K028 and K029 (Waste from the product steam stripper and Spent catalyst from the hydrochlorinator reactor in the production of 1,1,1-trichloroethane).

1. The commenter first questioned the Agency's characterization of 1,1,1-trichloroethane as a suspect carcinogen. The commenter argues that based on their evaluation of the available data, 1,1,1-trichloroethane has not been found to be carcinogenic (i.e., the commenter believes that the Agency has incorrectly assessed the data).

The Agency disagrees with the commenter's claim. Although the NCI Bioassay Study on the carcinogenicity of 1,1,1-trichloroethane referred to in the listing background document (pg. 464) and an unpublished study are inconclusive, positive responses in two in vitro systems (a rat embryo cell transformation assay (Price et. al. 1978) and a bacterial mutation assay (Simmon et. al. 1977; McCann and Ames, 1976)) currently used to detect chemical carcinogens, indicate that 1,1,1-trichloroethane has the potential for carcinogenicity in animals. Additionally, a two year carcinogenesis animal bioassay is being repeated at the National Cancer Institute. Therefore, the Agency believes that there is ample evidence

to consider 1,1,1-trichloroethane as a suspect carcinogen.\*  
The listing background document on trichloroethane production and the Health and Environmental Effects Profile on 1,1,1-Trichloroethane will be modified to discuss these findings.

2. The commenter then criticized the Agency's characterization of 1,1,1-trichloroethane as "very toxic to aquatic life" and noted that the toxicity levels reported do not warrant this characterization.

In re-evaluating the aquatic toxicity of 1,1,1-trichloroethane, the Agency agrees with the commenter that 1,1,1-trichloroethane is not sufficiently toxic to fish to warrant characterization as "very toxic ...". In the Registry of Toxic Effects (1975 Edition), a widely used reference book which is published by the National Institute for Occupational Safety and Health (NIOSH), a rating of the aquatic toxicity or non-toxicity of chemical substances is provided. In this rating, substances with an LC<sub>50</sub> of between 10,000 ug/l to 100,000 ug/l is considered slightly toxic [1,1,1-trichloroethane (96 hour LC<sub>50</sub> 26-58 mg/l)]. Therefore, the Agency will modify the listing background document to reflect this change.

The Agency will, however, continue to include 1,1,1-trichloroethane as a constituent of concern in this particular listing.

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\*It should be noted that the Agency recently determined to retain the listing of 1,1,1-trichloroethane as a toxic pollutant under §307(a) of the Clean Water Act. The reasons for that action are incorporated by reference herein.

### References

- McCann, J. and B. Ames. 1976. Detection of Carcinogens as Mutagens in the Salmonella Microsome Test. Assay of 300 chemicals: Discussion Proc. Nat. Acad. Sci. 78:950.
- Price, P. J. et. al. 1978. Transforming Activities of Trichloroethylene are Proposed Industrial Alternatives. In Vitro 14:290.
- Simmon, V. F. et. al. 1977. Mutagenic Activity of Chemicals Identified in Drinking Water in: Progress in Genetic Toxicology, ed. I. D. Scott, B. A. Bridges and F. H. Sobels. pp. 249-258. Elsevier.

## LISTING BACKGROUND DOCUMENT

## TRICHLOROETHYLENE AND PERCHLOROETHYLENE PRODUCTION

Column bottoms or heavy ends from the combined production of trichloroethylene and perchloroethylene (T)

Summary of Basis for Listing

The column bottoms or heavy ends from the combined production of trichloroethylene and perchloroethylene are generated when recycling streams from the chlorination and oxychlorination processes become contaminated and must be removed and disposed. The Administrator has determined that these heavy ends are solid wastes which may pose a present or potential hazard to human health and the environment when improperly transported, treated, stored, disposed of or otherwise managed and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following consideration:

- (1) The column bottoms or heavy ends from combined trichloroethylene and perchloroethylene production contain significant concentrations of 1,1,2,2-tetrachloroethane, hexachlorobutadiene, and hexachlorobenzene, each of which are carcinogenic. Also, 1,1,2,2-tetrachloroethane is a known mutagen. All of these substances are also toxic to aquatic life and bioaccumulate in living tissues. In addition, the waste contains smaller amounts of ethylene dichloride, hexachloroethane and 1,1,1,2 tetrachloroethane, all substances with carcinogenic and/or mutagenic properties.
- (2) A large quantity (a combined estimated total of at least 15,000 metric tons) of these wastes is generated annually.

- (3) The wastes are disposed of primarily through incineration or landfilling. Smaller amounts are deep well injected into limestone formations. If not managed properly, these hazardous contaminants could be emitted to the air from inadequate incineration or improper land disposal or leach from landfills and injection wells to expose humans and other life. The chlorinated organics 1,1,2,2-tetrachloroethane, hexachlorobutadiene, and hexachlorobenzene, as well as ethylene dichloride, are water soluble and therefore could migrate from the wastes to contaminate groundwater in concentrations sufficient to cause substantial hazard.

#### Industry Profile(1,2,3,4)

Perchloroethylene and trichloroethylene are produced in a combined process by seven companies at ten manufacturing locations primarily situated in the Texas and Louisiana Gulf area. The location of the facilities, their annual production capacity, and estimated 1979 production are shown in Table 1 and Figure 1. As shown in Table 1, the estimated 1979 production for perchloroethylene and trichloroethylene are 367,500 and 125,300 MT, respectively. The annual production levels for each individual plant are variable and range from 12,600 to 63,700 MT for perchloroethylene producers and 14,000 - 63,700 MT for manufacturers of trichloroethylene. Average annual per plant production figures are 36,750 MT for perchloroethylene and 41,400 MT for trichloroethylene.

There currently is excess capacity within this industry for both the production of perchloroethylene and trichloroethylene. Increased regulatory pressures from both the Environmental Protection Agency (EPA) and the Occupational Safety and Health

TABLE 1  
ESTIMATED CAPACITY AND PRODUCTION  
PERCHLOROETHYLENE AND TRICHLOROETHYLENE

COMPANY	LOCATION	1979 CAPACITY (MT/YR) <sup>B</sup>		1979 PRODUCTION (MT/YR)	
		PERCHLOROETHYLENE	TRICHLOROETHYLENE	PERCHLOROETHYLENE	TRICHLOROETHYLENE
Diamond Shamrock	Deer Park, TX	75,000	A	52,500	
Dow	Freeport, TX	68,000	68,000	47,600	47,600
	Pittsburg, CA	18,000		12,600	
	Plaquemine, LA	54,000		37,800	
Dupont	Corpus Christi, TX	73,000		51,100	
Ethyl	Baton Rouge, LA	23,000	20,000	16,100	14,000
PPG	Lake Charles, LA	91,000	91,000	63,700	63,700
Stauffer	Louisville, KY	32,000		22,400	
Vulcan	Geismar, LA	68,000		47,600	
	Wichita, KS	23,000		16,100	
	TOTAL	<u>525,000</u>	<u>179,000</u>	<u>367,500</u>	<u>125,300</u>

<sup>A</sup>23,000-MT/yr. capacity unit placed on standby in early 1978

<sup>B</sup>MT = Metric tons

SOURCE: References 1, 2, 3, 4

FIGURE 1  
 LOCATIONS OF PLANTS MANUFACTURING  
 PERCHLOROETHYLENE AND TRICHLOROETHYLENE



	<u>Chemicals Produced</u> <sup>*</sup>
1) Diamond Shamrock Corp., Deer Park, TX	A
2) Dow Chemical Co., Freeport, TX	A,B
3) Dow Chemical Co., Pittsburg, CA	A
4) Dow Chemical Co., Plaquemine, LA	A
5) DuPont, Corpus Christi, TX	A
6) Ethyl Corp., Baton Rouge, LA	A,B
7) PPG Industries, Inc., Lake Charles, LA	A,B
8) Stauffer Chemical Co., Louisville, KY	A
9) Vulcan Materials Co., Geismar, LA	A
10) Vulcan Materials Co., Wichita, KS	A

\* A = perchloroethylene, B = trichloroethylene

SOURCE: Reference 9

Administration (OSHA) are serving to inhibit future growth in demand for these chemicals. It is anticipated that short- and long-term growth will average 1-2% and that the industry output can be represented by a flat growth curve.

### Manufacturing Process(3)

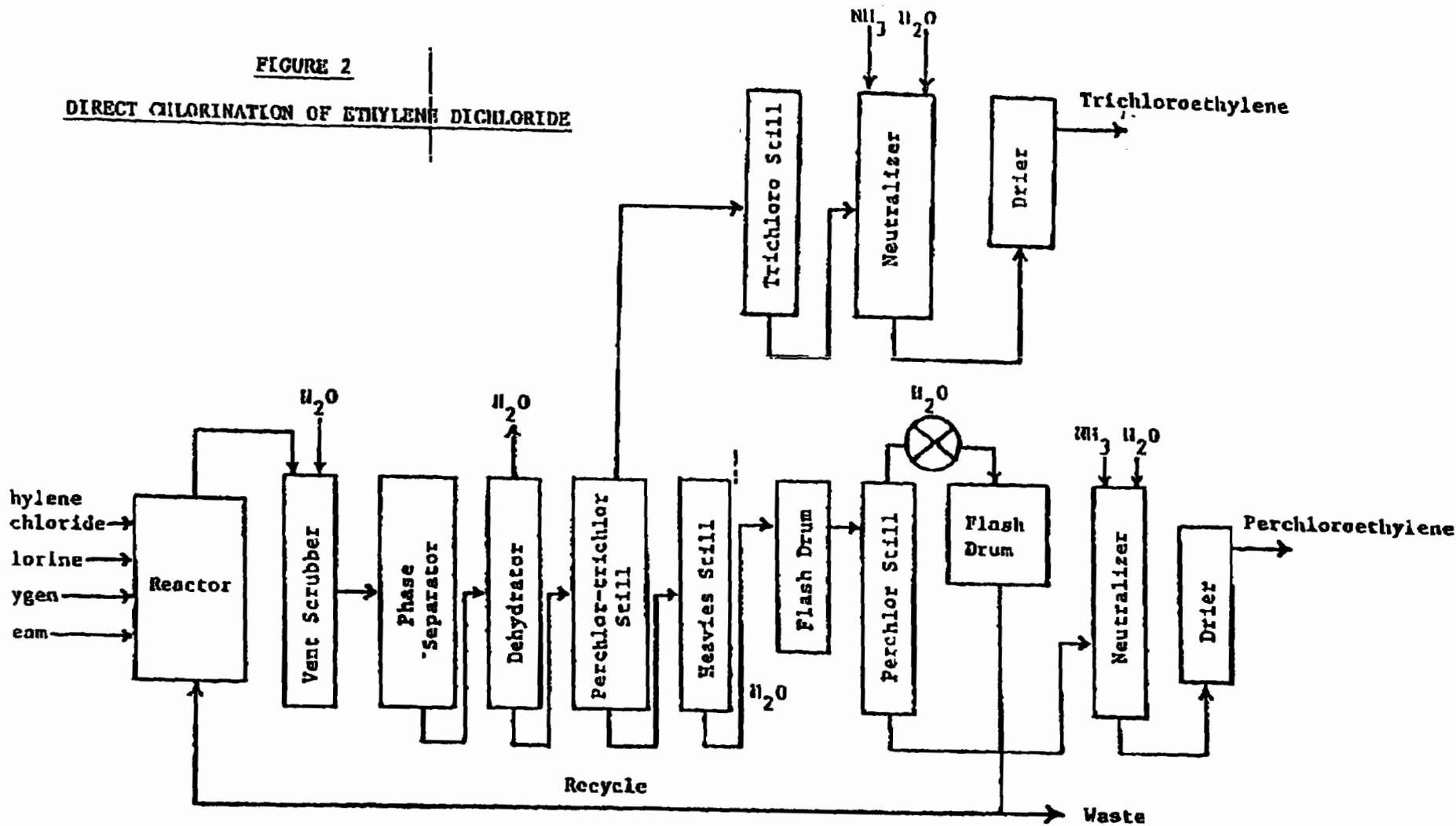
Perchloroethylene and trichloroethylene are produced either separately or as co-products by either the chlorination or oxychlorination of ethylene dichloride or other C<sub>2</sub>-chlorinated hydrocarbons. The ratio of raw material feed determines the relative yields of perchloroethylene and trichloroethylene. Perchloroethylene is also produced by the chlorinolysis of light hydrocarbons with by-product production of carbon tetrachloride.

This listing document covers wastes generated by the co-production process.

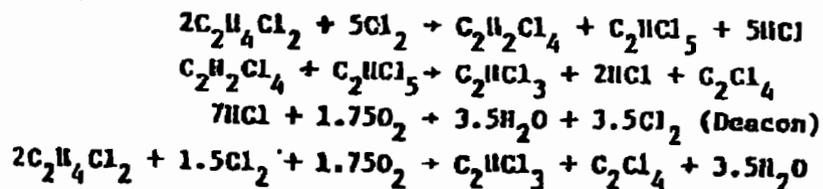
#### ° Direct Chlorination of Ethylene Dichloride (See Figure 2)

Perchloroethylene and trichloroethylene are produced by a single-stage oxychlorination process from ethylene dichloride and chlorine. Ethylene dichloride, chlorine, oxygen, and recycled chlorinated organics are fed to a fluid bed reactor. An inexpensive oxychlorination catalyst (e.g., copper chloride) is used and the reactor is maintained under pressure at about 425°C. Feed adjustments may be employed to vary product

**FIGURE 2**  
**DIRECT CHLORINATION OF ETHYLENE DICHLORIDE**



Reaction



85 to 90% yield

SOURCE: Reference 3.

560

ratios, depending upon producer requirements.

The condensed crude and weak acid are then phase-separated with the crude, being dried by azeotropic distillation. In the perchlor-trichlor column, the crude is split into two streams, one trichlor-rich and the other perchlor-rich. The perchlor-rich stream, containing midboilers and heavies, is fed to the heavies column where high boilers (1,1,2,2- and 1,1,1,2-tetrachloroethane, pentachloroethane, hexachloroethane, dimers, tar and carbon) are removed as bottoms and flashed to remove tars and carbon. Midboilers are concentrated in the overheads and recycled. Perchlor recovered from the bottoms of the still is neutralized with ammonia, washed, and dried.

The crude trichlor stream is fed to the trichlor product still, where low boilers, such as dichloroethylenes, are removed overhead and recycled to the reactor. Trichlor is removed from the bottom, neutralized with ammonia, washed, and dried.

This process description is an example of one of several processes for the manufacture of perchloroethylene and trichloroethylene from ethylene dichloride. Similar waste constituents (i.e., a range of chlorinated organic hydrocarbons, including 1,1,2,2-tetrachloroethane, hexachlorobutadiene, and hexachlorobenzene), are expected regardless of the process.

## Waste Generation and Management

### 1. Waste Generation

The column bottoms or heavy ends from the combined production of perchloroethylene and trichloroethylene can contain a wide variety of chlorinated hydrocarbons. A typical chemical composition for the waste stream, often referred as hex waste, is shown in Table 2 with composition presented in terms of weight and mole percent.(2,9) This information indicates that the primary constituents of the waste stream are 1,1,2,2-tetrachloroethane, hexachlorobutadiene, and hexachlorobenzene. (Table 2 also includes solubilities of the waste stream constituents.)(2,9,20)

The information presented in Table 2 was employed to calculate the expected quantities of each hazardous component which is generated on an annual basis. Personal communications(5,6,7) with selected chemical manufacturers and a review of the available literature indicate that the quantity of still bottoms which becomes contaminated and must be disposed can approach 3-5 percent of production. Assuming that these wastes are generated at a rate of 3% of production, the estimated quantity of each component is presented in Table 3. The estimated annual generation rates are shown to range from 88-4996 metric tons for the individual waste components.

### 2. Waste Management (5,6,7)

Additional information was collected to assess the current practices employed for handling these waste streams on an

TABLE 2  
TYPICAL COMPOSITION OF HEX-WASTES

	MOLE %	WEIGHT %	SOLUBILITY g/100g distilled water	in PPM*
Ethylene Dichloride	1.4	0.6	.80	8,000
beta-Trichloroethane	7.2	4.5	.50	5,000
Perchloroethylene	5.7	4.5	.01	100
1,1,1,2-Tetrachloroethane	7.9	6.3	.01	100
1,1,2,2-Tetrachloroethane	29.1	23.0	.29	2,900
Pentachloroethane	2.7	3.3	<.05	<500
Hexachlorobutadiene	27.5	33.8	.0000005	0.005
Hexachlorobenzene	14.9	20.0	<.05	<500
Hexachloroethane	<u>3.6</u>	<u>4.0</u>		Very low
TOTAL	100.0	100.0		

SOURCE: References 2,9

\* Converted to PPM, Value = g/100g x 10<sup>4</sup>

SOLUBILITY OF PARTICULAR HEX WASTE CONSTITUENTS

IN PPM (DISTILLED WATER)

Ethylene Dichloride	8,690
beta-Trichloroethane	4,500
Perchloroethylene	150 - 200
1,1,2,2-Tetrachloroethane	2,900
Hexachlorobutadiene	2
Hexachlorobenzene	0.006 - 0.020
Hexachloroethane	50

SOURCE: Reference 20

Table 3

PROJECTED QUANTITIES OF INDIVIDUAL HEX-WASTE COMPONENTS

	MOLE %	WEIGHT %	ANNUAL PRODUCTION (MT)
Hexachlorobutadiene	27.5	33.8	4,996
1,1,2,2-Tetrachloroethane	29.1	23.0	3,400
Hexachlorobenzene	14.9	20.0	2,956
1,1,1,2-Tetrachloroethane	7.9	6.3	931
Hexachloroethane	3.6	4.0	591
Ethylene Dichloride	1.4	0.6	88
Perchloroethylene	5.7	4.5	665
beta-Trichloroethane	7.2	4.5	665
Pentachloroethane	<u>2.7</u>	<u>3.3</u>	<u>448</u>
TOTAL	100.0	100.0	14,780

SOURCE: Estimate based on Table 2 and waste generation rate of 3% of production. (Waste streams are, however, subject to variation in terms of both composition and rate of generation.)

individual basis. The available information indicates that these wastes are either being incinerated or disposed of through landfill or deep well injection into limestone formations. Table 4 identifies the estimated quantities of waste being generated at each production facility and the current procedures for disposing of these wastes. As shown in Table 4, approximately 70% of the wastes are incinerated, with 22% going to landfill and 7% to deep well injection.

(NF)

#### Hazards Posed by Waste

As noted above, most of these hex wastes are incinerated. Inadequate incineration conditions -- i.e., temperature and residence times--can result in the airborne disposal of uncombusted chlorinated organics, partially combusted organics and newly formed organic compounds. Phosgene is an example of a partially combusted chlorinated organic which is produced by the decomposition or combustion of chlorinated organics by heat. (10,11,12) Phosgene has been used as a chemical warfare agent and is recognized as extremely toxic.

The landfilling of column bottoms or heavy ends in an unsecure land disposal facility may result in groundwater contamination caused by migration of the toxic chlorinated organics from the waste into the surrounding environment. The most carcinogenic wastestream pollutant, 1,1,2,2-tetrachloroethane, is highly soluble in water, as shown in Table 2. Ethylene dichloride, another carcinogen found in the wastestream, is even more soluble and thus would also tend to migrate

TABLE 4

WASTE GENERATION RATES AND MANAGEMENT PROCEDURES

<u>Company</u>	<u>Location</u>	<u>Waste Production MT</u>	<u>Current Disposal Practice</u>
Diamond Shamrock Corporation	Deer Park, TX	1,570	LF
Dow Chemical U.S.A.	Freeport, TX	2,850	I
	Pittsburg, CA	370	I
	Plaquemine, LA	1,130	I
E.I. DuPont de Nemours Company, Inc.	Corpus Christi, TX	1,530	I
Ethyl Corporation	Baton Rouge, LA	940	DWI
PPG Industries	Lake Charles, LA	3,820	I
Stauffer Chemical Company	Louisville, KY	670	LF
Vulcan Material Company	Geismar, LA	1,420	I
	Wichita, KS	<u>480</u>	I
	TOTAL	14,780	

I - Incineration  
DWI - Deep Well Injection  
LF - Landfill

SOURCE: References 5, 6, 7

~~-12-~~  
-516-

from the waste. The remaining chlorinated organics in the waste stream are also water soluble to some extent (see Table 2). These compounds also have demonstrated potential for mobility through soils and persistence in groundwater.(17) (See also information summarized at pp. 15-20 below.) Thus, it appears likely that hazardous constituents may escape from this waste stream and contaminate groundwater. There clearly is insufficient justification to warrant finding that waste constituents will not migrate into groundwater if improperly managed. It should be noted that many facilities generating these wastes are located in the Texas and Louisiana Gulf area (see Figure 1) where rainfall precipitation is heavy, so that the wastes are exposed regularly to solubilizing media.

Another problem with the landfilling of these wastes is the potential for these contaminants, particularly hexachlorobenzene, to volatilize into the surrounding atmosphere. An actual damage incident confirms this risk. In the Louisiana area in the early 1970's, hex wastes containing hexachlorobenzene (HCB), a relatively volatile material, were transported over a period of time to municipal landfills in uncovered trucks. High levels of HCB have since been reported in the blood plasma of individuals along the route of transport(8). In a sampling of 29 households along the truck route, the average plasma level of HCB was 3.6 ppb with a high of 23 ppb, while the average plasma level of HCB in a control group was 0.5 ppb with a high of 1.8 ppb (Farmer et. al., 1976).

Additionally, cattle in the surrounding area absorbed HCB in their tissue and 20,000 animals were quarantined by the State Department of Agriculture (Lazar 1975)(8).

The deep well injection of these wastes in permeable limestone formations is also practiced by the industry and could result in the migration of the hazardous constituents from the waste and present the same type of problems presented when these wastes are insecurely landfilled.

An additional reason for listing these wastes as hazardous are the large volumes generated annually. The estimated quantities of hex wastes disposed of by each producer range from 370 to 3,820 metric tons per year (Table 4). This is a significant quantity of waste disposal by individual generators in the same area. It is expected that producers will use the same disposal facility for long periods of time, causing more exposure over longer time periods to populations in the same disposal facility areas if wastes are improperly managed. Also, more exposure would be expected along prevalent migration and transport routes.

Additional health and environmental fate information on the listed constituents of concern is presented in the following section of this document. In general, this information indicates qualitatively that these constituents are sufficiently mobile and persistent to reach environmental receptors. In light of the extreme dangers to human health and the environment posed by these constituents, there is insufficient indication of environmental degradation to justify a failure to list this waste as hazardous.

## Health and Ecological Effects

### 1. Hexachlorobenzene (HCB)

Priority Pollutant - HCB is currently listed as a priority pollutant under Section 307(a) of the Clean Water Act.

Health Effects - Hexachlorobenzene (HCB) has produced cancers in animal species.(13,14) Other animal studies have shown that HCB crosses the placental barrier to produce toxic effects and fetal mortality.(15) Hexachlorobenzene is stored for long periods in body fat. Chronic exposure to HCB has been shown to result in damage to the liver and spleen.(16) It has also been demonstrated that at doses far below those which are lethal, HCB enhances the body's capability to toxify, rather than detoxify, other foreign organic compounds present in the body.(17)

Virtually all hexachlorobenzene emitted from an uncontrolled landfill is expected to persist in groundwater or reach surface waters via groundwater movement.(18) Such behavior is likely to result in exposure to humans using potable water supplies within the exposed adjacent areas.

The recommended ambient criterion(19) level for HCB in water is 1.25 nanograms per liter. Actual measurements, on the other hand, of finished drinking water in certain geographic areas have been measured at levels six times the recommended criterion designed to protect human health, demonstrating the mobility and persistence of the material (See Appendix A.)

Ecological Effects - Hexachlorobenzene is very persistent.(20) It has been reported to move through the soil into the groundwater.(21) Movement of hexachlorobenzene within surface water systems is projected to be widespread.(18) Movement to this degree will likely result in exposure to aquatic life forms in rivers, ponds, and reservoirs. Similarly, potential exposure to humans is likely where water supplies are drawn from surface waters.

Hexachlorobenzene is likely to contaminate accumulated bottom sediments within surface water systems and bioaccumulate in fish and other aquatic organisms.(18)

Regulatory Recognition of Hazard - As indicated in Appendix A, hexachlorobenzene is a chemical evaluated by CAG as having substantial evidence of carcinogenicity. Ocean dumping of hexachlorobenzene is prohibited. An interim food contamination tolerance of 0.5 ppm has been established by FDA.

Additional information on the adverse effects of hexachlorobenzene can be found in Appendix A.

## 2. Hexachlorobutadiene (HCBd)

Priority Pollutant - Hexachlorobutadiene is a priority pollutant under Section 307(a) of the CWA.

Health Effects - Hexachlorobutadiene (HCBd) has been found to be carcinogenic in animals.(22) Upon chronic exposure to animals by the DOW Chemical Company and others, the kidney appears to be the organ most sensitive to HCBd.(22,23,24,25) The recommended human health criterion level for this compound

in water, is .77 ppb. (See 44 Fed. Reg. 15926, 15954 (March 15, 1979).)

Virtually all HCBD emitted from the waste management scenario described previously is expected to persist in groundwater or reach surface waters via groundwater movement.(18) Such behavior is likely to result in exposure to humans using such groundwater sources as drinking water supplies within adjacent areas.

Ecological Effects - Movement of HCBD within surface water systems is projected to be widespread.(18)

HCBD is likely to contaminate accumulated bottom sediments within surface water systems and is likely to bioaccumulate in fish and other aquatic organisms.(18)

The USEPA (1979) has estimated that the BCF is at 870 for the edible portion of fish and shellfish consumed by Americans.

Hexachlorobutadiene is persistent in the environment.(20) It has been reported to move through soil into groundwater from Hooker Chemical's Hyde Park waste disposal site,\* and thus is mobile enough to migrate from improperly managed landfills into the environment.

Industrial Recognition of Hazard - Hexachlorobutadiene is considered to have a high toxic hazard rating via both oral and inhalation routes (Sax, Dangerous Properties of Industrial Materials).

Additional information on the adverse effects of hexa-

\*OSW Hazardous Waste Division, Hazardous Waste Incidents, Unpublished, Open File, 1978.

chlorobutadiene can be found in Appendix A.

### 3. Hexachloroethane

Priority Pollutant - Hexachloroethane is a priority pollutant under Section 307(a) of the CWA.

Health Effects - Hexachloroethane has been reported to be carcinogenic to animals, meaning that humans may be similarly affected.(27) Humans exposed to vapors at low concentrations for short periods have had liver, kidney and heart degeneration and central nervous system damage.(28)

Virtually all hexachloroethane emitted from a landfill is expected to persist in groundwater or reach surface waters via groundwater movement.(18) Such behavior is likely to result in exposure to humans using such groundwater sources as drinking water supplies within adjacent areas.

Ecological Effects - Movement of hexachloroethane within surface water systems is projected to be widespread.(18) Movement to this degree will likely result in exposure to aquatic life forms in rivers, ponds, and reservoirs.

Hexachloroethane is likely to be released to the atmosphere from surface water systems.(18)

Regulatory Recognition of Hazard - OSHA has set a TWA for hexachloroethane at 1 ppm (skin). Measurements of this compound in finished drinking water have shown that hexachloroethane occurs at least at the recommended water criterion level,(28) confirming that this compound may persist in

dangerous concentrations.

Additional information on the adverse effects of hexachloroethane can be found in Appendix A.

#### 4. Tetrachloroethanes

Priority Pollutant - Both 1,1,1,2-tetrachloroethane and 1,1,2,2-tetrachloroethane are designated as priority pollutants under Section 307(a) of the CWA.

Health Effects - 1,1,2,2-Tetrachloroethane has been shown to produce liver cancer in laboratory mice.(29) In addition, passage of 1,1,1,2-tetrachloroethane across the placental barrier has been reported.(30) In an Ames Salmonella bioassay, 1,1,2,2-tetrachloroethane was shown to be mutagenic.(31) Occupational exposure of workers to 1,1,2,2-tetrachloroethane produced neurological damage, liver and kidney ailments, lung edema and fatty degeneration of the heart muscle.(32)

Ecological Effects - Freshwater invertebrates are sensitive to 1,1,2,2-tetrachloroethane with a lethal concentration of 7-8 mg/l being reported.(33) USEPA estimates the RCF to be 18.(33)

Regulations - OSHA has set the TWA at 5 ppm (skin) for 1,1,2,2-tetrachloroethane.

Additional information on the adverse effects of tetrachloroethanes can be found in Appendix A.

#### 6. Ethylene Dichloride

Priority Pollutants - Ethylene dichloride (1,2-dichloroethane) is designated as a priority pollutant under Section 307(a) of

the CWA.

Health Effects - Ethylene dichloride has been shown to cause cancer in laboratory animals.(34) In addition, this compound and several of its metabolites are highly mutagenic.(35) Ethylene dichloride crosses the placental barrier and is embryotoxic and teratogenic.(36,37,38,39,40) It has also been shown to concentrate in milk.(41) Exposure to this compound can cause a variety of adverse health effects including damage to the liver, kidneys and other organs. It can also cause internal hemorrhaging and blood clots.(42)

Regulatory Recognition of Hazard - OSHA has set the TWA at 50 ppm. The Office of Air, Pollution and Noise has completed a preregulatory assessment for ethylene dichloride under Sections 111 and 112 of the Clean Air Act. Preregulatory assessments are also being conducted by EPA's Office of Water and Waste Management under the Safe Drinking Water Act and by the Office of Toxic Substances under the Toxic Substances Control Act.

Industrial Recognition of Hazard - Sax in Dangerous Properties of Industrial Materials rates ethylene dichloride as highly toxic upon ingestion and inhalation.

Additional information on the adverse effects of ethylene dichloride can be found in Appendix A.

## References

1. Chemical Profiles. Schnell Publishing Company, Inc., New York. 1979.
2. U.S. EPA. Emission control options for the synthetic organic chemicals manufacturing industry: carbon tetrachloride and perchloroethylene. U.S. EPA, Office of Air Quality Planning and Standards. Contract Number 68-02-2257. March, 1979.
3. Lowenheim, F. A., and M.K. Moran. Faith, Keyes, and Clark's industrial chemicals, 4th Ed. Wiley Interscience, New York. 1975.
4. U.S. EPA. Assessment of industrial hazardous waste practice: organic chemicals, pesticides, and explosives. EPA No. SW-118c. NTIS PB No. 251 307. January, 1976.
5. Personal communication with Dr. H. Farber, Dow Chemical Company, Midland, Michigan, February 1980.
6. Personal communication with Mr. Perry Norling, DuPont Co., Wilmington, Delaware, February, 1980.
7. Personal communication with Dr. Frederick C. Dehn, PPG Industries, Pittsburgh, Pennsylvania, February, 1980.
8. U.S. EPA. Open files. Hazardous Site Control Branch, WH-548. U.S. EPA, 401 M St., S.W., Washington, D.C. 20460. Contact Hugh Kaufman. (202) 245-3051.
9. U.S. EPA. Emission control options for the synthetic organic chemical manufacturing industry: 1,1,1-trichloroethane product report. U.S. EPA, Office of Air Quality Planning and Standards, Contract Number 68-02-2577. July, 1979.
10. Edwards, J.B. Combustion formation and emission of traces species. Ann Arbor Science. 1977.
11. NIOSH. Criteria for a recommended standard: Occupational exposure to phosgene. HEW, PHS, CDC, NIOSH. NTIS PB No. 267 514. 1976.
12. Cabral, J. R. P., et al. Carcinogenic activity of hexachlorobenzene in hamsters. Tox. Appl. Pharmacol. 41:155 1977.

13. Cabral, J.R.P., et al. Carcinogenesis study in mice with hexachlorobenzene. Toxicol. Appl. Pharmacol. 45:323. 1978.
14. Grant, D.L., et al. Effect of hexachlorobenzene on reproduction in the rat. Arch. Environ. Contam. Toxicol. 5:207. 1977.
15. Grant, D.L., et al. Effect of hexachlorobenzene on reproduction in the rat. Arch. Environ. Contam. Toxicol. 5:207. 1977.
16. Koss, G., et al. 1978. Studies on the toxicology of hexachlorobenzene. III. Observations in a long-term experiment. Arch. Toxicol. 40:285. 1978.
17. Carlson, G.P. Induction of cytochrome P-450 by halogenated benzenes. Biochem. Pharmacol. 27:361. 1978.
18. U.S. EPA. Technical support document for aquatic fate and transport estimates for hazardous chemical exposure assessments. U.S. EPA. Environmental Research Lab. Athens, Georgia. 1980.
19. U.S. EPA. Chlorinated benzenes: Ambient water quality criteria. NTIS PB No. 297 919. 1979.
20. U.S. EPA. Water-related environmental fate of 129 priority pollutants. EPA No. 440/4-79-029b. 1979.
21. Zoeteman, B.C.J. Persistent organic pollutants in river water and ground water in the Netherlands. In Proceedings; Third International Symposium on Aquatic Pollutants. Jekyll Island, Georgia. October 15-17, 1979.
22. Kociba, R.J. Results of a two-year chronic toxicity study with hexachlorobutadiene in rats. Amer. Ind. Hyg. Assoc. 38:589. 1977.
23. Kociba R.J., et. al. Toxicologic study of female rats administered hexachlorobutadiene or hexachlorobenzene for 30 days. DOW Chemical Company. 1971.
24. Schwetz, et. al. Results of a reproduction study in rats fed diets containing hexachlorobutadiene. Toxicol. Appl. Pharmacol. 42:387. 1977.
25. Schroit, et. al. Kidney lesions under experimental hexachlorobutadiene poisoning. Aktual, Vpo. Gig. Epidemiol. 73. CA:81:73128F (translation). 1972.
26. Not used in text.

27. National Cancer Institute. Bioassay of hexachloroethane for possible carcinogenicity. No. 78-1318. NTIS PB No. 282 608/AS. 1978.
28. U.S. EPA. Chlorinated ethanes: Ambient water quality criteria. NTIS PB No. 297 920. 1979.
29. National Cancer Institute. Bioassay of 1,1,2,2-tetrachloroethane for possible carcinogenicity. U.S. Department of Health, Education and Welfare, Public Health Service, National Institutes of Health, National Cancer Institute, DHEW Publication No. (NIH) 78-827. NTIS PB No. 277 453/AS. 1978.
30. Truhaut, R., N.P. Lich., H.T. Dutertre-Catella, G. Molas, and V.N. Huyen. Toxicological study of 1,1,1,2-tetrachloroethane. Archives des Maladies Professionnelles, de Medecine du Travail et de Securite 35(6):593608. 1974.
31. Brem, H., et al. The mutagenicity and DNA-modifying effect of haloalkanes. Cancer Res. 34:2576. 1974.
32. National Institute for Occupational Safety and Health. Criteria for a recommended standard...occupational exposure to 1,1,2,2-tetrachloroethane. U.S. Department of Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, DHEW (NIOSH) Publication No. 77-121. NTIS PB No. 273 802. December, 1976.
33. U.S. EPA. Chlorinated ethanes: Ambient water quality criteria. NTIS PB No. 297 920. 1979.
34. National Cancer Institute. Bioassay of 1,2-dichloroethane for possible carcinogenicity. U.S. Department of Health, Education and Welfare, Public Health Service, National Institutes of Health, National Cancer Institute, Carcinogenesis Testing Program, DHEW Publication No. (NIH) 78-1305. NTIS PB No. 285 968. January, 1978.
- 35a. McCann, J., E. Choi, E. Yamasaki, and B. Ames. Detection of carcinogens as mutagenic in the Salmonella/microsome test: Assay of 300 chemicals. Proc. Natl. Acad. Sci. USA 72(2):5135-5139. 1975.
- 35b. McCann, J., V. Simmon, D. Streitwieser, and B. Ames. Mutagenicity of chloroacetaldehyde, a possible metabolic product of 1,2-dichloroethane (ethylene dichloride), chloroethanol (ethylene chlorohydrin), vinyl chloride, and cyclophosphamide. Proc. Nat. Acad. Sci. 72(8): 3190-3193. 1975.

36. Vozovaya, M. Changes in the estrous cycle of white rats chronically exposed to the combined action of gasoline and dichloroethane vapors. Akush. Genekol. (Kiev) 47(12):65-66. 1971.
37. Vozovaya, M. Development of offspring of two generations obtained from females subjected to the action of dichloroethane. Gig. Sanit. 7:25-28. 1974.
38. Vozovaya, M. The effect of low concentrations of gasoline, dichloroethane and their combination on the generative function of animals and on the development of progeny. Gig. Tr. Prof. Zabol. 7:20-23. 1975.
39. Vozovaya, M. The effect of low concentrations of gasoline, dichloroethane and their combination on the reproductive function of animals. Gig. Sanit. 6: 100-102. 1976.
40. Vozovaya, M. The effect of dichloroethane on the sexual cycle and embryogenesis of experimental animals. Akusk. Ginekol. (Moscow) 2:57-59. 1977.
41. Urosova, T.P. (About a possibility of dichloroethane absorption into milk of nursing women when contacted under industrial conditions.) Gig. Sanit. 18(3):36-37. 1953 (Rus).
42. Parker, J.C., et al. Chloroethanes: A review of toxicity. Amer. Ind. Hyg. Assoc. J. 40:A46-60. March, 1979.
43. Not used in text.

## **Pesticides**

## LISTING BACKGROUND DOCUMENT

## MSMA AND CACODYLIC ACID PRODUCTION

## By-product Salts Generated in the Production of MSMA and Cacodylic Acid. (T)

I. Summary of Basis for Listing

The hazardous waste generated in the production of MSMA (monosodium methanearsonate) and cacodylic acid is an arsenic-contaminated salt by-product. The Administrator has determined that the solid waste from MSMA and cacodylic acid production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. These wastes contain very substantial concentrations of arsenic, which is an extremely toxic heavy metal. Arsenic has also been shown to be carcinogenic, mutagenic, and teratogenic. The waste generated at one plant was contaminated with arsenic at a concentration of 6300 mg/l.
2. Large quantities of arsenic-contaminated wastes are generated annually in the production of MSMA and cacodylic acid. Furthermore, large quantities are often disposed of at individual sites. Approximately 190,000,000 lbs of arsenic-contaminated salt have been stored in an open, uncovered pile in Wisconsin.
3. In mildly reducing environments, prevailing in most shallow groundwaters, arsenic is most likely to be present as the very toxic arsenite, to be relatively mobile, and to persist virtually indefinitely.
4. Several incidents of environmental contamination have occurred due to the leaching of MSMA/cacodylic acid wastes disposed of in landfills, resulting in adverse human health effects.

## II. Sources of the Waste

A. Profile of the Industry - MSMA is used primarily as a herbicide, and is also an intermediate in the production of cacodylic acid. MSMA is produced in the U.S. by Diamond Shamrock (Green Bayou, Texas); Crystal Chemical (Houston, Texas); and Vineland Chemical (Vineland, New Jersey). Estimated production of MSMA in 1974 was 35 million pounds.<sup>(1)</sup> Both Crystal Chemical and Vineland Chemical also manufacture cacodylic acid which results in a similar arsenic-contaminated salt by-product. Combination of the salt by-products from both the manufacture of MSMA and cacodylic acid probably occurs at most manufacturing sites, a supposition could not be confirmed for all sites.\*

B. Manufacturing Process and Waste Composition - The manufacture of MSMA involves the reaction of arsenic trioxide and liquid caustic soda to form sodium arsenite. This solution of arsenite is then reacted with methyl chloride to form a disodium methylarsenate (DSMA) slurry. This slurry is concentrated, cooled and centrifuged with the DSMA cake going to acidifying tanks and the liquid going to storage for reuse. The DSMA cake is then acidified to form monosodium methylarsenate (MSMA). This slurry is concentrated, cooled and centrifuged, with the monosodium methylarsenate in the liquid phase being transferred to a formulating tank, and the resulting salt cake being collected for disposal. The final MSMA product is formulated to various strengths and is shipped in either bulk form or containers. Arsenic is present in the salt by-product

\*Crystal Chemical evidently combines its two waste streams, since its state disposal permit provides for disposal of the combined waste streams.

in substantial concentrations, since it is a prevalent feedstock constituent. The production scheme for MSMA is depicted in Figure 1.

The manufacture of cacodylic acid involves the reduction of MSMA using sulfur dioxide. This reduced MSMA is neutralized with caustic soda and then reacted with methyl chloride to form cacodylic acid. The cacodylic acid is concentrated, cooled and centrifuged. The cacodylic acid in the liquid phase goes to a formulating tank and the salt cake is collected for disposal. Again, it is reasonable to expect that arsenic is heavily concentrated in the waste because it is a dominant feedstock constituent.

The presence of arsenic in the waste in high concentrations is confirmed by an analysis of MSMA salt cake waste generated by Crystal Chemical and provided to the Texas Department of Water Resources. This analysis indicates that the waste contains arsenic concentrations of 6,300 mg/l (6). The National Interim Primary Drinking Water Standard for arsenic, a standard regulatory benchmark for measuring arsenic contamination in drinking water, is .05 mg/l, demonstrating the significant concentration level of arsenic in the waste stream.\*

The Agency does not presently possess waste concentration data for cacodylic acid waste, but arsenic concentrations are similarly believed to be high, in light of arsenic presence as an essential feedstock material. Further, it is believed that the MSMA and cacodylic acid wastes are often combined for disposal (see page 2), again suggesting that the waste streams will contain substantial concentrations of arsenic.

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\*With regard to the comparison of waste concentrations and the Drinking Water Standards, which assume environmental release, although not all the arsenic contained in the waste is likely to be released from the waste into the environment, arsenic in these wastes may well be released in concentrations well above .05 mg/l. (see p. 2 following).

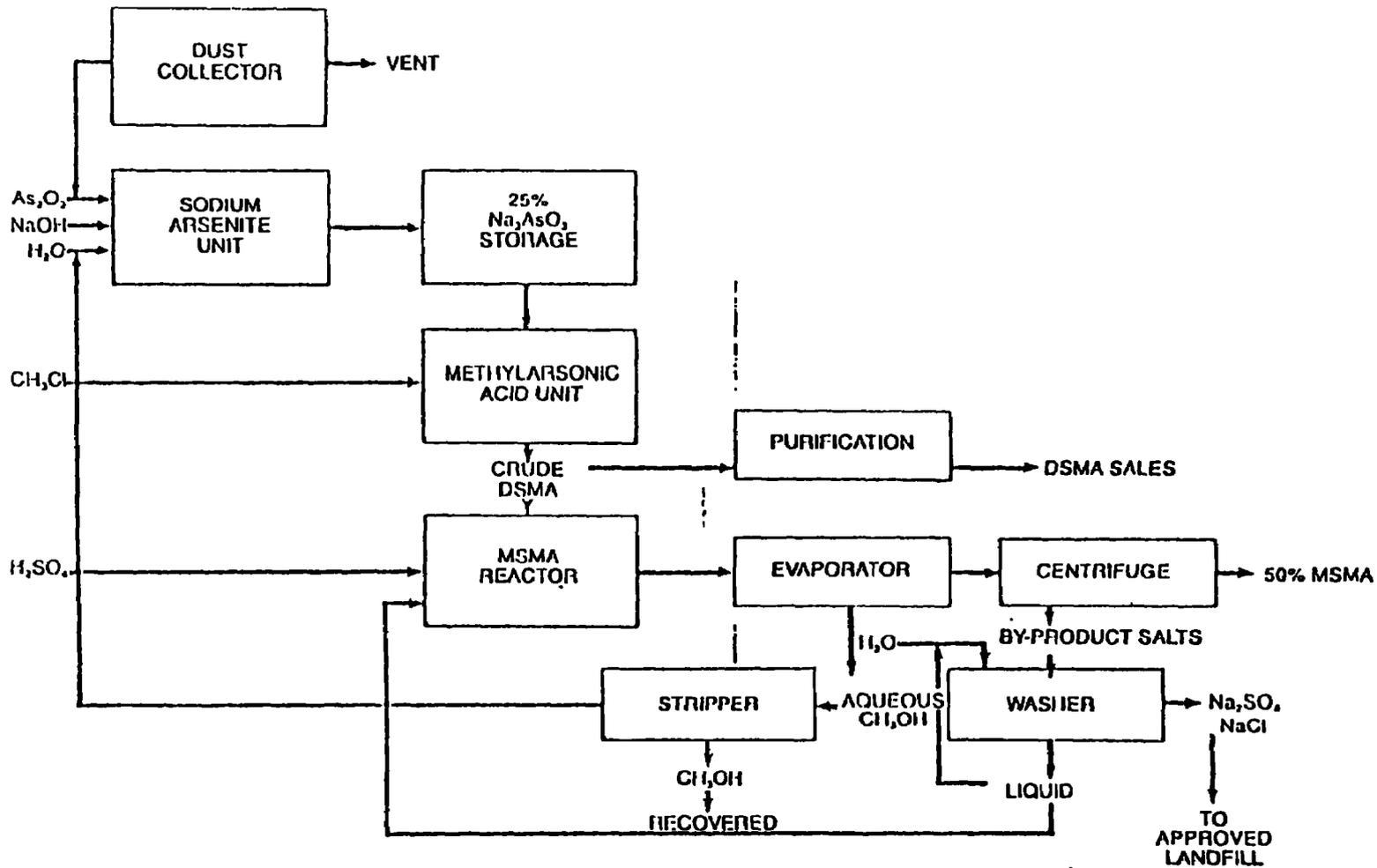


Figure 1. PRODUCTION AND WASTE SCHEMATIC FOR MSMA.

(3)

C. Waste Generation and Management Practices and Quantities of Wastes Managed

There are a number of waste management practices in current industry use, which are discussed below. In addition to these described practices, however, there is a history of waste mismanagement resulting in environmental harm. Descriptions of damage incidents resulting from mismanagement of these wastes are set forth at pp. 6-7 following.

Vineland Chemical has disposed of its solid waste in several landfills in Pennsylvania. In May, 1979, Vineland received a permit from the State of Pennsylvania to dispose of 3,000 tons of arsenic contaminated waste.<sup>(4)</sup>

Diamond Shamrock has a permit from the Texas Department of Water Resources to dispose a monthly average of 481 tons of solid waste from the production of various compounds.<sup>(5)</sup>

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\* (2)

Crystal Chemical has a state permit for deepwell injection of MSMA-cacodylic acid solid wastes which are slurried with liquid wastes and rainwater and are injected 3500 to 4500 feet below the surface in the Frio Formation (Attachment I). Prior to obtaining this permit, the company utilized unlined earthen holding ponds for waste management in combination with an off-site disposal program in commercial facilities.

III. Discussion of Basis for Listing

A. Hazards Posed by the Waste

The Agency has a number of reasons for listing these wastes

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\*The underlined data are those obtained from proprietary reports and data files

as hazardous. First, these waste streams have been implicated in a number of actual damage incidents, demonstrating the potential for substantial hazard if these wastes are improperly managed.

Second, the concentrations of arsenic contained in these wastes are very significant, so that if even a small percentage of the arsenic escapes from the waste, it will enter the environment in high enough concentrations to cause substantial harm. Further, arsenic is likely to be mobile, and will be highly persistent upon escaping from the waste, thus increasing the likelihood of it reaching receptors in concentrations sufficient to cause a substantial hazard. Certainly, there is insufficient evidence to indicate that arsenic will not migrate from the waste, and in light of the known dangers of this contaminant and its high concentrations in the waste, such assurance is necessary to justify not listing these wastes.

Finally, these wastes contain large quantities of arsenic (as well as high concentrations), and wastes containing large quantities of arsenic are often disposed of at individual sites, thus increasing the likelihood of a major damage incident.

#### 1. Incidents Involving Mismanagement of These Wastes.

A history of mismanagement of solid waste from the manufacture of MSMA and cacodylic acid has been documented. It has been reported that Ansul Company, a former manufacturer of MSMA and other arsenical compounds, has stored 95,000 tons of arsenic-contaminated salt on company property in Marinette, Wisconsin. Until recently, this stockpile

was left open to the weather with no containment of runoff. The State of Wisconsin Department of Natural Resources has ordered Ansul to cover the pile as an interim measure and to truck the waste to a landfill in Illinois. (28)

A report from the files of the Texas Department of Water Resources (Attachment I) indicates that a landfill containing these waste streams was subject to overflow conditions during high rainfall periods, causing waste washout, soil contamination, and potential leaching hazard. The report indicates that elevated levels of arsenic were detected to "depths of several feet" in soil surrounding the landfill. This could result in the leaching of arsenic into groundwater and potable water supplies.

## 2. Hazards Based on Arsenic Concentrations in These Wastes and Likely Environmental Fate of Released Wastes

As noted above, arsenic is present in these waste streams in very high concentrations. Thus, improper management of these wastes, for example in unlined landfills, could easily result in a substantial hazard to human health and the environment, in light of the health hazards posed by arsenic (see pp. 9-11 following).

Two likely exposure pathways for the leaching of arsenic are into groundwater and surface water. The potential for this to occur from a waste/soil matrix depends on the concentration of arsenic in the soil, soil type (clay, sand, loam, etc.), the soil pH, as well as the concentrations of cadmium, magnesium, iron, and aluminum in the soil. Arsenic is not easily leached in fine-textured soils (clay materials) but may be leached downward in sandy or loam soils. (30)

Once arsenic escapes from these wastes and migrates to groundwater, it can be expected to be both mobile and persistent. Thus, in mildly reducing environments present in most shallow groundwaters, arsenic is most likely to be present in the form of arsenite, a mobile and highly toxic compound.<sup>(7)</sup> As an elemental heavy metal, arsenic will persist in some form virtually indefinitely.

The propensity for arsenic to migrate through soil and groundwater and to persist is illustrated by an arsenic poisoning incident occurring in Minnesota in 1972.<sup>(8)</sup> In this case, eleven persons became seriously ill by drinking water from a well 31 feet deep. Water from this well was found to contain up to 21,000 mg/l of arsenic. The source of the arsenic was established to be some 50 pounds of arsenic-containing grasshopper bait buried in a seven foot trench near the well about 40 years previously.

Significant pollution of groundwater by arsenic moving from the La Bounty landfill in Iowa has also been noted recently<sup>(9)</sup>, and the potential for movement of this element through the soil profile has been illustrated by its appearance in increased concentration in groundwater at a land treatment site for municipal wastewater.<sup>(10)</sup>

A second exposure pathway of concern is surface water. These wastes, unless properly managed to prevent washout or runoff, could easily contaminate surface waters. Indeed, two of the incidents described above illustrate potential surface water contamination as a result of improper management of these wastes (Attachments I and II).

### 3. Quantities of the Waste Generated

MSMA and cacodylic acid by-product salts are generated in large

concentrations, and also are disposed of in large quantities at individual sites. The above described damage incident from Marinette, Wisc., indicates that 95,000 tons of these wastes were stored (improperly) at a single site. Similarly, Vineyard disposes of 3,000 tons of these wastes each year.<sup>(4)</sup> Obviously, such large quantities of this hazardous constituent has the propensity for large-scale environmental harm--for instance, there is a greater chance of exposure, and that environmental leaching will continue for longer periods. The large quantities of waste generated is thus a further reason for listing these wastes.

## B. Health and Ecological Effects

### 1. Arsenic

Health Effects - Arsenic is extremely toxic in animals and humans<sup>(11)</sup>. Death in humans has occurred following ingestion of very small amounts (5mg/Kg) of this chemical<sup>(12)</sup>. Several epidemiological studies have associated cancers with occupational exposure to arsenic<sup>(13-15)</sup>, including those of the lung, lymphatics and blood<sup>(16,17)</sup>. Certain cases involving a high prevalence of skin cancer have been associated with arsenic in drinking water<sup>(18)</sup>, while liver cancer has developed in several cases following ingestion of arsenic<sup>(19)</sup>. Results from the administration of arsenic to animals in drinking water or by injection supports the carcinogenic potential of arsenic.

Occupational exposure to arsenic has resulted in chromosomal damage<sup>(20)</sup>, while several different arsenic compounds have demonstrated positive mutagenic effects in laboratory studies<sup>(21-23)</sup>.

The teratogenicity of arsenic and arsenic compounds is well established <sup>(24-26)</sup> and includes defects of the skull, brain, kidneys,

gonads, eyes, ribs and genito-urinary system.

The effects of chronic arsenic exposure include skin diseases progressing to gangrene, liver damage, neurological disturbances<sup>(27)</sup> and cardiovascular disease<sup>(13)</sup>.

Arsenic is designated as a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of arsenic can be found in Appendix A.

Ecological Effects - The data base for the toxicity of arsenic to aquatic organisms is more complete for freshwater organisms, where concentrations as low as 128 ng/l have been acutely toxic to freshwater fish. A single marine species produced an acute value in excess of 8,000 ng/l. Based on one chronic life cycle test using Daphnia magna, a chronic value for arsenic was estimated at 853 ng/l.<sup>(28)</sup>

Bioaccumulation factors can reach 13,000 in oysters, 8,600 in lobsters, and 23,000 in mussels.<sup>(28)</sup>

Regulations - OSHA has set a standard air TWA of 500 mg/m<sup>3</sup> for arsenic. DOT requires a "poison" warning label.

The Office of Toxic Substances under FIFRA has issued a pre-RPAR. The Carcinogen Assessment Group has identified arsenic as a compound which exhibits substantial evidence of carcinogenicity. The Office of Drinking Water has regulated arsenic under the Safe Drinking Water Act due to its toxicity and the Office of Air Quality Planning and Standards has begun a preregulatory assessment of arsenic based on its suspected carcinogenic effects. The Office of Water Planning and Standards under Section 304(a) of the Clean Water Act has begun development of a regulation based on

health effects other than on carcinogenicity and environmental effects. Finally, the Office of Toxic Substances has completed Phase I assessment of arsenic under TSCA.

In addition, the states of Pennsylvania, Texas, and Wisconsin obviously deem this waste to require careful management to prevent substantial environmental harm (see attachment I and II).

Industrial Recognition of Hazard - Arsenic is rated as highly toxic through intra-muscular and subcutaneous routes in Sax, Dangerous Properties of Industrial Materials.(29) Arsenic is also rated as highly toxic through ingestion, inhalation, and percutaneous routes in Patty, Industrial Hygiene and Toxicology.

V. References

1. U.S. EPA. Kelso, G., R. Wilkinson, J. Malon, Jr., and T. Ferguson. Development of information on pesticides manufacturing for source assessment. EPA No. 600/2-78-100. Environmental Protection Agency, Research Triangle Park, NC. NTIS PB No. 283 051/1BE. 1978.
2. Not used in text.
3. Sittig, M. Pesticides process encyclopedia. Noyes Data Corporation, Park Ridge, New Jersey. 1977.
4. Personal Communication, Kirti Shah, Pennsylvania Department of Environmental Resources (717-787-7381), 1/31/80. See Appendix D.
5. Personal Communication, David Barker, Texas Department of Water Resources. (512-475-5633), 12/18/79. See Appendix D.
6. Personal communication, David Jeffrey, Texas Department of Water Resources (512-475-7097), 12/31/79. See Appendix D.
7. NIOSH. Registry of toxic effects of chemical substances. U.S. Government Printing Office. Washington, D.C. 1978.
8. U.S. EPA. The Report to Congress: Waste disposal practices and their effect on groundwater. U.S. EPA, Office of Water Supply, Office of Solid Waste Management Programs. NTIS PB No. 265 081. January 1977.
9. Koerner, E. L., and D. A. Haws. Long-term effects of land application of domestic wastewater. EPA No. 600/2-79-072. U.S. EPA, Washington, D.C. NTIS PB No. 297 501/9BE. 1979.
10. Hounslow, A. W. Ground-water geochemistry: arsenic in landfills. Ground Water 18:331. July-August 1980.
11. Gleason, M. N., et al. Clinical toxicology of commercial products. Acute poisoning, 3rd ed., p. 76. The Williams and Wilkins Company, Baltimore. 1969.
12. Lee, A. M. and Fraumeni, J. F., Jr. Arsenic and respiratory cancer in man: An occupational study. Jour. Natl. Cancer Inst. 42:1045. 1969.
13. Pinto, S. S. and B.M. Bennett. Effect of arsenic trioxide exposure on mortality. Arch. Environmen. Health 7:5883. 1963.
14. Kwratune, M., et al. Occupational lung cancer among copper smelters. Int. Jour. Cancer 13:552. 1974.

15. Ohn, M. G., et al. Respiratory cancer and occupational exposure to arsenicals. Arch. Environ. Health 29:250. 1974.
16. Baetjer, A. M., et al. Cancer and occupational exposure to inorganic arsenic. 18th Int. Cong. Occup. Health. Brighton, England. p. 393. In: Abstracts, September 14-19. 1975.
17. Tseng, W. P., et al. Prevalence of skin cancer in an endemic area of chronic arsenicism in Taiwan. Jour. Natl. Cancer Inst. 40:453. 1968.
18. ECAO Hazard Profile: Arsenic. SRC, Syracuse, NY. 1980.
19. Nordenson, I., et al. Occupational and environmental risks in and around a smelter in northern Sweden. II. Chromosomal aberrations in workers exposed to arsenic. Hereditas 88:47. 1978.
20. Petres, J., et al. Zum Einfluss a norgan ischen Arsens auf die DNS-Synthese menschlicher Lymphocyten in vitro. Arch. Derm forsch. 242:343. 1972.
21. Paton, G. R. and A.C. Allison. Chromosome damage in human cell cultures induced by metal salts. Mutat. Res. 16:332. 1972.
22. Moutshcen, J. and N. Degraeve. Influence of thiol-inhibiting substances on the effects of ethyl methyl sulphonate on chromosomes. Experientia 21:200. 1965.
23. Hood, R. D. and S.L. Bishop. Teratogenic effects of sodium arsenate in mice. Arch. Environ. Health 24:62. 1972.
24. Beandoin, A. R. Teratogenicity of sodium arsenate in rats. Teratology 10:153. 1974.
25. Ferm, V. H., et al. The teratogenic profile of sodium arsenate in the golden hamster. Arch. Environ. Health 22:557. 1971.
26. U.S. EPA. Arsenic: Ambient water quality criteria. NTIS PB No. 292 420/7BE. 1979.
27. WHO. Environmental health criteria: arsenic. World Health Organization. Geneva. 1979.
28. Sperling, L. Wisconsin's Hazardous Waste Line, Wisconsin Natural Resources. 4 (1): 14-16. 1980.
29. Sax, N. Irving. Dangerous properties of industrial materials. 4th ed. Van Nostrand Reinhold, New York. 1975.
30. National Academy of Science, National Research Council. Arsenic. PB No. 2604. 1977.

## ATTACHMENT I

Plant located in West Harris County. Crystal manufactures arsenic-based pesticide chemicals for sale. The proposed well will be used to dispose of water which has been contaminated as a result of these manufacturing processes. To the present time, the Company has utilized only unlined earthen holding ponds for wastewater management, in combination with a program of off-site disposal in commercial waste facilities. Efforts to minimize the volume of contaminated waste water in the Company's ponds by evaporation, are thwarted by the heavy rainfalls which occur in the Houston area. Site inspection after such rainfall typically reveals that water, tinged an orange-brown color, covers much of the site, and in some instances, slowly drains off-site. Analyses of soil samples from the plant indicate elevated levels of arsenic compounds in the soil to depths of several feet. To prevent further soil and water pollution, the Company has undertaken the waste disposal well project as the most environmentally safe method of plant waste disposal. Along with the implementation of the proposed injection operations, it will be necessary to correct the existing pollution by closing the ponds, and diking and paving the plant area. Effective control of rainfall runoff will prevent off-site discharge of arsenic-contaminated waters. Evaluation of the disposal well project plans follow.

### CHARACTERISTICS AND COMPOSITION OF THE WASTE WATER

Manufacturing Process - Listed below is a summary of operations at Crystal's RogerJale Road facility.

MSMA - Arsenic trioxide and liquid caustic soda are reacted to form sodium arsenite. This solution of sodium arsenite is then reacted with methyl chloride to form a DSMA (disodium methylarsenate) slurry. This slurry is concentrated, cooled and centrifuged with the DSMA cake going to acidizing tanks and the liquid going to storage for reuse. The DSMA cake is acidized to form monosodium methylarsenate. This slurry is concentrated, cooled and centrifuged with the monosodium methylarsenate in the liquid phase being transferred to a formulating tank, and the resulting salt cake being collected for disposal. The final MSMA product is formulated to various strengths and is shipped in either bulk form or containers.

Dinitro General - Dinoseb (2-Sec-Butyl-4, 6-Dinitrophenol) is dissolved in a solvent, an emulsifier is added, and the product is shipped in either bulk or containers.

Dinitro 3 - Dinoseb is reacted with triethanolamine to form the triethanolamine salt of Dinoseb. A surfactant is added and the material is shipped in bulk or containers.

Naptalam - Alphanaphthyl amine and phthalic anhydride are reacted in a closed system to form sodium naphthylphthalamate. This material is one of the ingredients of a product produced under the trade name NAPTRO.

Naptro - Naptalam, caustic soda, and Dinoseb are mixed to form NAPTRO. This material is solid in 5 gallon and in 30 gallon containers.

Dimethoate 267 - Technical dimethoate is dissolved in a solvent and emulsifiers are added. The product is then either drummed at the plant or shipped in bulk form to a packager.

Cacodylic Acid - MSMA is reduced using sulfur dioxide. This reduced MSMA is neutralized with caustic soda and then reacted with methyl chloride to form cacodylic acid. The cacodylic acid is concentrated, cooled and centrifuged with the cacodylic acid in the liquid phase going to a formulating tank and the salt cake collected for disposal.

Chemical Analysis - Samples from the Company's existing waste water holding ponds have yielded the following analysis.

	<u>MSMA Salt Cake</u>	<u>Wastewater (Pond)</u>	<u>Wastewater (Sump)</u>
pH	7.9	9.8	9.4
Total Residue (105°C)	30%	7.7%	5,100 mg/l
Alkalinity, as CaCO <sub>3</sub>			
Hydroxyl	0 mg/l	3,000 mg/l	0 mg/l
Bicarbonate	1,800	0	220
Carbonate	3,920	8,000	1,080
Chloride	78,000	20,800	850
Nitrate N	0.60	0.26	0.16
Sulfate	103,000	11,600	564
Total Organic Carbon	2,400	2,000	180
Metals			
Arsenic	6,300	6,900	1,500
Barium	<0.5	<0.5	<0.5
Boron	<0.02	0.08	0.08
Cadmium	4.6	0.13	<0.01
Calcium	116	85	24
Chromium	26	5	0.6

Treatability Studies - Various alternative methods of disposal and treatment of the waste streams have been investigated. While some of these various methods could be marginally successful in eliminating the waste, each produces contaminated sludge or residue. Therefore, deep well injection is judged to be the most practical and economic solution for disposal of this waste stream.

The following methods were investigated as an alternative to injection:

1. Solar evaporation - The efficiency of solar evaporation is related to temperature, humidity and rainfall rate, among other factors. The annual rainfall rate at the plant site is in excess of 50" per year while the evaporation rate is approximately 43" per year. Evaporation would also produce a concentrated, contaminated precipitate which would pose additional disposal problems.

2. Stream stripping - Little, if any, of the contaminants would be removed and an extremely high level of energy consumption would be required.

3. Spray evaporation - Spray evaporation, while more effective than solar ponds, will also be inefficient because of the humid climatic conditions. Spray evaporation has a potential for air pollution and will produce a contaminated sludge. Large surface areas would be required for this type of system and these areas are not available at the plant site.

**ATTACHMENT II**

**PHONE LOG**

MEMORANDUM OF ORAL ADVICE

Bureau of Solid Waste Management  
Division of Hazardous Waste Management  
State of Pennsylvania  
Department of Environmental Resources

Date: January 31, 1980

Name: Kurti Shah, 717-787-7381

Re: Vineland Chemical Solid Waste  
(MSMA & Cacodylic Acid)

Telephone  Conference

Facts and Query: \_\_\_\_\_

Quantity, Composition and Present and Past Disposal Practices for  
Disposal of MSMA and Cacodylic Acid Waste in Pennsylvania.

Is this information Public Record? Yes.

Answer: Disposed of in past at Grove Sanitary Landfill (used a process  
developed by Stobatrol Corporation to encapsulate waste. Monitoring  
wells in area show high sulfates and chlorides. No arsenic yet.  
State may order recovery of waste) and at Lyncott Landfill (uses  
terra-tite system).

By: E.C. Monnig

Comments: Waste is said to be 60% NaCl, 40% Na<sub>2</sub>SO<sub>4</sub> and less than 1%  
arsenic (according to Vineland). Vineland permitted to dispose of  
1,000 tons (850 yd<sup>3</sup>) in August, 1977. May 1979 - permit to dump 2,000-  
3,000 pounds of solid waste from MSMA and Cacodylic Acid production.

MEMORANDUM OF ORAL ADVICE

Date: December 18, 1979

Name: David Barker, TDWR 512-475-5633

Re: MSMA Waste - Diamond Shamrock Telephone  Conference

Facts and Query: Quantity, Composition and Disposal practices of MSMA  
solid waste -- Diamond Shamrock.

Answer: Waste contains NaCl-Na<sub>2</sub>SO<sub>4</sub> and arsenic. Relative concentration  
unknown. Diamond Shamrock permitted to dispose on-site and off-site.  
Off-site permit allows 481 tons on a monthly average.

By: E.C. Monnig

Comments: \_\_\_\_\_  
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\_\_\_\_\_  
\_\_\_\_\_

MEMORANDUM OF ORAL ADVICE

Date: December 31, 1979

Name: David Jeffrey TDWQ

Re: Cacodylic Acid and MSMA Waste Telephone  Conference

Facts and Query: 1) Is the Crystal Chemical Solid waste report a matter of public record? Yes.

2) Does MSMA salt also contain Cacodylic Acid by-products? Probably.

Answer: \_\_\_\_\_

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By: E.C. Monnig

Comments: \_\_\_\_\_

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## LISTING BACKGROUND DOCUMENT

### CHLORDANE PRODUCTION

Wastewater and Scrub Water from the Chlorination of Cyclopentadiene in the Production of Chlordane (T)

Wastewater Treatment Sludges from the Production of Chlordane (T)

Filter Solids from the Filtration of Hexachlorocyclopentadiene in the Production of Chlordane (T)

Vacuum stripper discharges from chlordane chlorinator in the production of chlordane (T)

#### I. SUMMARY OF BASIS FOR LISTING

The hazardous waste streams generated from chlordane production include process wastewater and scrubwater, wastewater treatment sludge, filter solids, and vacuum stripper discharges. These waste streams contain hexachlorocyclopentadiene, chlordane, heptachlor, and other chlorinated organics.

The Administrator has determined that the solid waste from chlordane production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA.

This conclusion is based on the following considerations:

1. Wastewater and scrubwater from the chlorination of cyclopentadiene, wastewater treatment sludge and filter solids from hexachlorocyclopentadiene filtration contain hexachlorocyclopentadiene. Hexachlorocyclopentadiene is very toxic.
2. The vacuum stripper discharges from chlordane chlorinator waste is expected to contain chlordane, heptachlor, and other chlorinated organics. Chlordane and heptachlor have been reported to be carcinogenic and/or mutagenic.

3. \_\_\_\_\_\*

4. If the wastes are mismanaged, the toxic constituents in the waste could migrate from the waste and contaminate groundwater. Certain constituents of the waste (e.g., chlordane and heptachlor) are projected to be persistent in groundwater.

## II. SOURCES OF THE WASTE AND TYPICAL DISPOSAL PRACTICES

### A. Profile of the Industry

According to SRI Directory of Chemical Producers<sup>(1)</sup> and two other sources<sup>(2,3)</sup>, chlordane is produced by only one company, Velsicol Chemical Company (a subsidiary of Northwest Industries) at a plant in Marshall, Illinois. The chlordane industry production capacity is estimated at 13,600 metric tons/yr (15,000 tons/yr).<sup>(3)</sup> \_\_\_\_\_

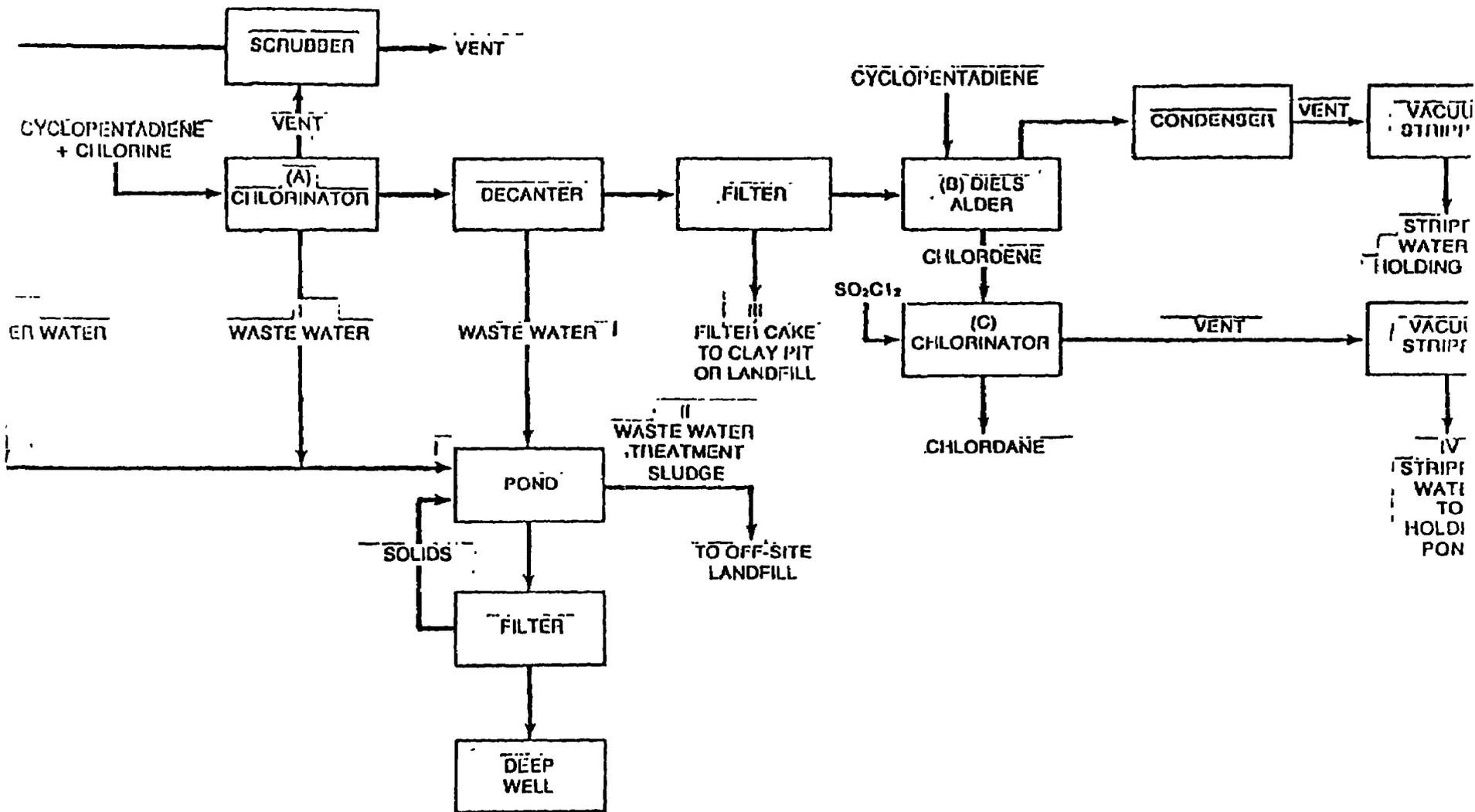
\_\_\_\_\_  
(4)

Chlordane is a versatile, broad-spectrum insecticide which has been in commercial use for more than 20 years.<sup>(3)</sup> It is used to protect a large variety of food crops, lawns, turf, ornamental and shade trees, and the like from parasitic insect life. In 1972, nonagricultural uses of chlordane accounted for an estimated 80 percent of total U.S. consumption of chlordane in that year.<sup>(3)</sup>

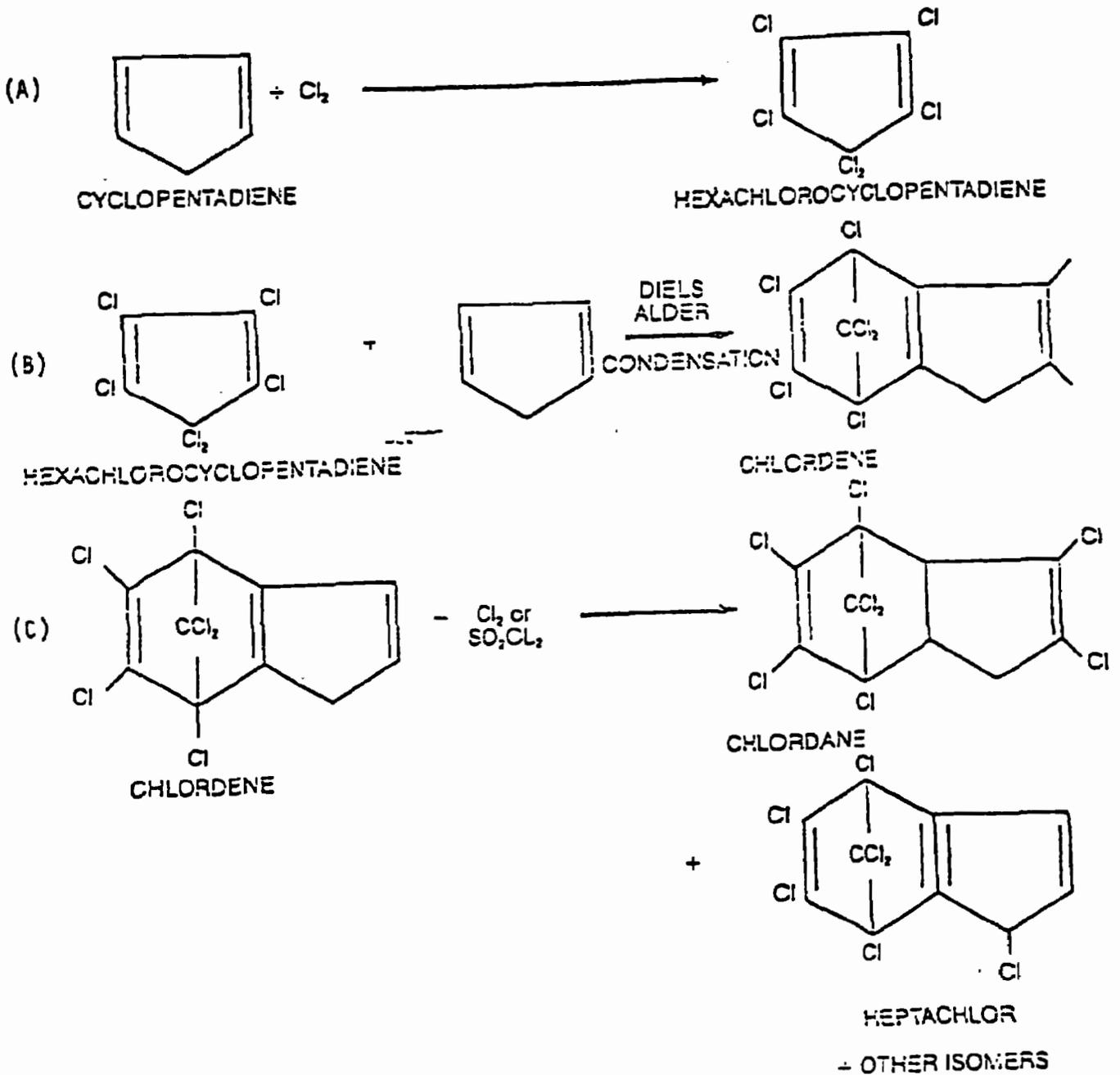
### B. Manufacturing Process

Figure 1 presents a generalized production and waste schematic for chlordane. As shown in Figure 1, the first production step involves chlorination of cyclopentadiene to

\* All underlined information is from proprietary reports and data files.



to obtain hexachlorocyclopentadiene. The hexachlorocyclopentadiene is then condensed with cyclopentadiene to form chlordene via the Diels Alder reaction. The chlordene is chlorinated to form chlordane. The main process reactions are as follows:(3)



These process reactions indicate the sources of the hazardous constituents in the wastes. They are marked A, B and C in Figure 1 to illustrate precisely where the reactions take place in the process.

### C. Waste Generation and Management

#### 1. Waste Streams

The four waste streams from the production of chlordane which are listed as hazardous are:

- ° Wastewater and scrub water from the chlorination of cyclopentadiene
- ° Wastewater treatment sludges
- ° Filter solids from the filtration of hexachlorocyclopentadiene
- ° Vacuum stripper discharges from chlordane chlorinator in the production of chlordane

Hexachlorocyclopentadiene is the constituent of concern in the first three listed wastes; chlordane, heptachlor, and other chlorinated organics are the constituents in the last listed waste.

Each of the wastes--wastewater and scrubwater, wastewater sludges, filter solids and vacuum stripper discharges--are marked I, II, III and IV respectively, in Figure 1.

Wastewater and scrubwater (I) are generated during the chlorination of cyclopentadiene and subsequent separation steps.

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will be present in this waste, probably in significant concentrations. This solid waste is sent to a commercial landfill for disposal. (3)

Vacuum stripper wastewater (IV) from the chlordane chlorinator vent vacuum scrubber contains chlordane (which would not be completely stripped) and heptachlor (the principal reaction product) in dissolved or suspended states. This waste goes to a holding pond prior to treatment.(3)

While the precise concentration of waste constituents in these waste streams are not presently available, even very small concentrations are of concern due to these compounds' extreme toxicity and capacity for genetic harm, as well as the history of waste mismanagement associated with the sole producer of chlorodane (see pp. 12-13 below). In any case, concentrations of these waste constituents are probably quite substantial, since the identified waste constituents are either principal reaction by products (hexachlorocyclopentadiene, heptachlor), or the end product (chlordane).

### III. DISCUSSION OF BASIS FOR LISTING

#### A. Hazards Posed by the Wastes

As previously mentioned, the listed wastes contain one or more of the hazardous constituents hexachlorocyclopentadiene, chlordane and heptachlor.

Chlordane and heptachlor have been well documented as having lethal effects in humans when ingested in small amounts, and hexachloropentadiene has been documented to alter kidney

functions, and cause eye and throat irritation and headache in humans. (For further information, see Health and Ecological Effect of Constituents pp. 14-18.)

1. Risks in Waste Management

As previously indicated, (Figure 1), the wastewaters from chlordane manufacture are discharged to a holding pond and filtered prior to disposal.<sup>(3)</sup> Sludges from this holding pond and filter solids from hexachlorocyclopentadiene filtration are taken off-site for disposal.<sup>(3)</sup> Disposal of the latter in landfills, even if plastic-lined drums are used, represents a potential hazard if the landfill is improperly designed or operated (i.e., drums corrode in the presence of even small amounts of water). This can result in the leaching of hazardous compounds and the subsequent contamination of groundwater. The holding pond presents a comparable risk if not properly managed.

Further, damage incidents indicate (see Damage Incidents, pp. 10-14) that hexachlorocyclopentadiene and heptachlor contaminated wastes have been disposed of in improperly designed and managed disposal facilities, which resulted in the contamination of the air and drinking water in the area. The possibility of improper management of these wastes and the resulting associated hazard, is thus highly realistic.

A further consideration is the actual transportation of these wastes to off-site disposal facilities. This increases the likelihood of their being mismanaged, and may result

either in their not being properly handled during transport or in their not reaching their destination at all (thus making them available for harm elsewhere). A transport manifest system combined with designated standards for the management of these wastes will greatly reduce their availability to do harm to human beings and the environment. In reference to this particular consideration, there was a damage incident in Memphis, Tennessee (discussed in detail on p. 12), due to similar, unmanifested waste being illegally transported and disposed.

2. Fate of Constituents in Waste Stream

The waste constituents appear to be fully able to migrate, pass through soils, and persist in the environment to an extent which could cause substantial harm to human health and the environment. Although heptachlor and chlordane are relatively insoluble, their ability to migrate has been demonstrated by documented damage incidents (see pp. 10-14). Based upon estimates by EPA,<sup>(6)</sup> the constituents chlordane and heptachlor in these waste streams are projected to be persistent in ground water, and exposure to humans using drinking water drawn from ground water in areas adjacent to disposal sites is likely. Movement of all the constituents identified in the waste stream is projected to be widespread within surface water systems, resulting in likely exposure to aquatic life forms in rivers, ponds, and reservoirs. Concentrations up to 0.8 mg/l and 0.04 mg/l of chlordane and

heptachlor respectively, have been observed in surface waters, confirming these compounds' mobility and persistence.(7,8)

Chlordane is a persistent chlorinated hydrocarbon insecticide. It persists in the soil for more than one year, sometimes for many years. Its overall rate of degradation is low.(29)

Further damage incidents (see Damage Incidents, below) illustrate that hexachlorocyclopentadiene and heptachlor have posed a hazard via air exposure to workers in contaminated areas; they have also migrated from disposal sites to surface and ground waters resulting in the contamination of drinking water sources in the vicinity.

### 3. Damage Incidents

The most serious wastewater and solid waste disposal problems from the manufacture of chlordane result from the synthesis of the hexachlorocyclopentadiene intermediate. The wastes from this process step contain highly toxic hexachlorocyclopentadiene reaction product. The link between disposal and management of heptachlorocyclopentadiene contaminated wastes and the hazardous implications of the leaching of the toxic organic into drinking water and/or air is well documented by the damage incident described below. Further, the vacuum stripper discharges from the chlordane chlorinator are of particular concern to the Agency because there also have been documented damage incidents which show the mis-

management, mobility and persistence of heptachlor contaminated waste streams (also described below).

Sometime during March, 1977, an unknown toxic substance began entering the Morris Forman waste treatment plant in Louisville Kentucky. As a result, employees on sight suffered from eye, nose, throat, lung, and skin irritation. It was found that many wastewaters from this plant contained constituents that are toxic. One of the predominant contaminants identified was hexachlorocyclopentadiene. Upon an investigation to determine the point of entry of these contaminants into the sewer system, it was found that a local waste handler had storage facilities for industrial wastes in the Louisville area. An investigation of five sights suspected to be used by the local disposal company confirmed the existence of hexachlorocyclopentadiene at one or more of the locations. Drums out in the open, buried drums and barrel storage were some of the implemented storage facilities and thus the points of release of these contaminants. As a result, towns whose water comes directly from the Ohio River had been alerted to the flow of raw sewage containing the contaminant hexachlorocyclopentadiene into the river at Louisville. Many of these toxic constituents were thus available for release due to improper management and disposal practices and even in minimal concentrations, may cause a potential health or environmental hazard via air exposure or contamination of drinking water sources. (2R)

Further, the same type of waste as the toxic heptachlor reaction by-products from chlordane production was generated by Velsicol in Memphis, Tennessee in the production of heptachlor. This waste material from the Memphis plant was one of the industrial wastes which was illegally dumped into the Louisville, Kentucky sewer by a contract waste disposal company. Again, the specific results were the killing of all sewage treatment plant biota and a resulting water contamination problem. The cost of decontamination was in excess of one million dollars and many workers were exposed to this toxic material.\*

Velsicol's Memphis plant has also created groundwater contamination problems resulting in several wells becoming contaminated following disposal of highly toxic heptachlor containing waste.\* Disposal of this waste in either deep wells or even in clay-lined pits can, and has, resulted in contamination problems.

In another serious instance of waste mismanagement involving both hexachlorocyclopentadiene containing wastes and Velsicol. Velsicol buried chlorinated pesticide waste containing hexachlorocyclopentadiene in drums at a Hardenman County site beginning in 1964. A U.S.G.S. Study (1966-1967) revealed that the wastes had migrated vertically to a depth of 90 feet and laterally to a distance of 25 feet. Hexachlorocyclopentadiene and other chlorinated hydrocarbons were also

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\* OSW Hazardous Waste Division, Hazardous Waste Damage Incidents, unpublished, open file 1978.

detected in surface runoff. Samples of adjacent water wells taken in April-May of 1978 showed contamination by the wastes. The contamination was sufficient to advise the well owners not to drink the water. At the time of the report a line was being laid to connect these owners with the Town County Water Supply. The cost of cleaning up the damage was \$741,000 plus an outlay of \$120,000 to supply water for the residents. (Source: United State Geological Survey (1966-1967); OSW Hazardous Waste Division, Hazardous Waste Incidents, unpublished, open file, 1978). This damage incident again illustrates the hazardousness of the waste, since upon mismanagement, waste constituents (including hexachlorocyclopentadiene) proved capable of migrating, persisting, and causing substantial hazard.

Past waste management practices of waste containing the constituents of concern have presented special problems. (For a more detailed discussion, see the report on Hazardous Waste Disposal, Subcommittee on Oversight and Interstate and Foreign Commerce, 96th Congress 1st sess. 4,10,17). As stated there, 16.5 million gallons of waste contaminated with heptachlor, endrin, benzene, and aldrin was dumped at a Hardenman County dump site. The dump site was ordered closed by the State of Tennessee in 1972, but local drinking is contaminated and unusable. This further indication of waste mismanagement by the sole producer of chlordane production wastes confirms the need for hazardous waste designation of these wastes.

Thus, these damage incidents illustrates the potential

environmental and health hazard resulting from leaching contaminants from these improperly disposed and managed wastes.

B. Health and Ecological Effects of Constituents

1. Chlordane

Health Effects - Chlordane is a very toxic chemical [oral rat LD<sub>50</sub> = 283 mg/Kg] with lethal effects in humans when ingested in small amounts.(9) Chlordane administered orally in mice is carcinogenic causing liver cancers in both sexes.(10) Chlordane has also been evaluated by CAG as having substantial evidence of carcinogenicity. Chlordane has been mutagenic in certain human cell assays.(11) Repeated doses of chlordane have altered blood protein, blood glucose and certain enzymes in gerbils.(12)

Chlordane is designated as a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on adverse effects of chlordane can be found in Appendix A.

Ecological Effects - Chlordane is acutely toxic to most aquatic animal life. Lethal concentrations to freshwater fish are in the microgram/liter range. Invertebrates appear to be more sensitive to chlordane.(13) Similarly, salt water fish and invertebrates have been shown to be very sensitive to chlordane.(14) Chronic aquatic toxicity of this compound is even more severe across all freshwater and

marine animal life.(14) In particular, fish embryos appear to suffer devastating damage from as little as a tenth of a microgram of chlordane.(14) The aquatic damage is amplified by the bioaccumulation factor of chlordane, i.e., scuds bioaccumulate chlordane 7,400 fold, freshwater algae bioaccumulate 133,000 fold. Chlordane is slightly toxic to birds, moderately toxic to wild mammals, highly toxic to soil insects, and moderately toxic to some soil bacteria and to earthworms.

Regulations - The OSHA standard for amounts of chlordane in air is a TWA of 600 n/m<sup>3</sup> (skin), based on the "one hit" model of chemical carcinogenesis. The USEPA has estimated levels of chlordane in ambient water which will result in a risk of 10<sup>-6</sup> cancer incidence of 0.12 nanograms/liter. Presently, a limit of 3 nanograms/liter for chlordane has been suggested under the Interim Primary Drinking Water Standard. The Canadian Drinking Water Standard is also 3 nanograms/liter. To protect freshwater life, the 24-hour average is 0.24 micrograms/liter and may not exceed 0.36 micrograms/liter. For saltwater species, the draft criterion is 0.0091 micrograms/liter for a 24-hour average, not to exceed 0.18 micrograms/liter.(15)\*

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\*The Agency is not using the proposed water quality criteria as a regulatory benchmark, but is referring to them here to illustrate a potential substantial hazard if it migrates from the waste at small concentrations.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, designates chlordane as highly toxic systematically via oral, skin absorption and inhalation routes of exposure.

2. Heptachlor

Health Effects - Heptachlor is extremely toxic in animals [oral rat LD<sub>50</sub> = 40 mg/Kg], also causing deaths in humans following ingestion of very small amounts.(16) Heptachlor is carcinogenic, causing liver cancer in mice.(17) Heptachlor has also been evaluated by CAG as having substantial evidence of carcinogenicity.

This chemical is mutagenic and teratogenic in animals, causing resorption of fetuses(18), chromosomal abnormalities in bone marrow cells in adults, and cataracts in offspring.(19) Heptachlor has caused a marked decrease in litter size and lifespan in newborn rats.(20) It also causes abnormal DNA synthesis in human cell cultures.(32)

Heptachlor is a convulsant(21) and also interferes with glucose metabolism when administered in chronic studies.(22) Additional information and specific references on adverse effects of heptachlor can be found in Appendix A.

Regulations - The OSHA standard for heptachlor is TWA (air) 500mg/m<sup>3</sup>.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, designates heptachlor as highly toxic via oral and dermal routes.

#### IV. References

1. Stanford Research Institute. 1977 Directory of Chemical Producers. SRI International, Menlo Park, California. 1977.
2. Farms Chemical Magazine. Farms Chemical Handbook. Meister Publishing Company, Willoughby, Ohio. 1977.
3. Von Rumker, et al. Production, distribution, use and environmental impact potential of selected pesticides. U.S. EPA Office of Pesticide Programs. EPA No. 540/1-74-001. 1975.
4. Proprietary information submitted to EPA by Velsicol Chemical Company through 1978 response to "308" letter.
5. Clement Associates, Inc. Dossier on hexachlorocyclopentadiene. Contract No. EA8AC013, prepared for TSCA Interagency Testing Committee. Washington, D.C. August, 1978.
6. U.S. EPA. Aquatic fate and transport estimates for hazardous chemical exposure assessments. U.S. Environmental Protection Agency, Environmental Research Laboratory. Athens, Georgia. February, 1980.
7. Pesticide Monitoring Journal. 8:33. 1974.
8. Pesticide Monitoring Journal. 3:124. 1969.
9. U.S. DHEW. Clinical Handbook on Economic Poisons. HEW, PHS, CDC. Atlanta, GA. NTIS PB No. 218 287. 1963.
10. National Cancer Institute. Bioassay of chlordane for possible carcinogenicity. NCI-CG-TR-8. NTIS PB No. 271 977. 1977.
11. Ahmed, F. E., et al. Pesticide-induced DNA damage and its repair in cultured human cells. Mutat. Res. 42:161. 1977.
12. Karel, A. K. and S.C. Saxena. Chronic chlordane toxicity: Effect on blood biochemistry of Meriones hurrianae Jerdon, the Indian desert gerbil. Pestic. Biochem. Physiol. 6:111. 1976.
13. U.S. EPA. Chlordane hazard profile (Draft). 1979.
14. Kats, M. Acute toxicity of some organic insecticides to three species of salmonids and to the threespine stickleback. Trans. Am. Fish. Soc. 90:264. 1961.

15. U.S. EPA. Chlordane: Ambient water quality criteria (draft). NTIS PB No. 292 425. 1979.
16. Gleason, M.N., et al. Clinical toxicology of commercial products. Acute Poisoning. 3rd ed. Williams and Wilkins Co. Baltimore. 1969.
17. U.S. EPA. Risk assessment of chlordane and heptachlor. Carcinogen Assessment Group. U.S. Environmental Protection Agency. Washington, D.C. 1977.
18. Cerey, K., et al. Effect of heptachlor on dominant lethality and bone marrow in rats. Mutat. Res. 21:26. 1973.
19. Mestitzova, M. On reproduction studies on the occurrence of cataracts in rats after long-term feeding of the insecticide heptachlor. Experientia 23:42. 1967.
20. Ahmed, F. E., et al. Pesticide-induced DNA damage and its repair in cultured human cells. Mutat. Res. 42:161. 1977.
21. St. Omer, V. Investigations into mechanisms responsible for seizures induced by chlorinated hydrocarbon insecticides: The role of brain ammonia and glutamine in convulsions in the rat and cockeral. Jour. Neuroceue. 18:365. 1971.
22. Kacew, S. and R.L. Singhal. The influence of p.p<sup>1</sup>-DDT, and chlordane, heptachlor and endrin on hepatic and renal carboxyhydrate metabolism and cyclic AMP-adenyl cyclase system. Life Sci. 13:1363. 1973.
23. NIOSH. Registry of toxic effects of chemical substances. 1978.
24. Morse, D. H. et al. Occupation exposure to hexachlorocyclopentadiene: How safe is sewage? JAMA 241:2177-2179. 1979.
25. Goggelman, W., et al. Mutagenicity of chlorinated cyclopentadiene due to metabolic activation. Biochem. Pharmacol. 27:2927-2930.
26. Winteringham, P. Chemical residues and pollution program of the Joint Division of the International Atomic Energy Agency and the Food and Agriculture Organization of the United Nations. Ecotoxicol. Environ. Safety 1:407-25. 1977.
27. Spechar, R. L., et al. Toxicity and bio-accumulation of hexachlorocyclopentadiene, hexachloronorborene, and heptachloroborene in larval and early juvenile fathead minnows. Bull. Environ. Contam. Toxicol. 21:576-83.

28. Control of Hazardous Material Spills. In Proceedings;  
The 1978 National Conference on Control of Hazardous  
Material Spills. Miami Beach, Florida. April 11-13, 1978.
29. Dawson, English, Petty, Physical chemical properties  
of hazardous waste constituents. 1980.

## LISTING BACKGROUND DOCUMENT

## DISULFOTON PRODUCTION

Wastewater Treatment Sludges from the Production of Disulfoton (T)

Still Bottoms from Toluene Reclamation Distillation in the Production of Disulfoton (T)

1. SUMMARY OF BASIS FOR LISTING

The organic waste streams from disulfoton production contain a variety of intermediate products which are toxic (i.e., toluene and o,o,o-triethyl ester of phosphorodithioic acid).

The Administrator has determined that the solid waste from disulfoton production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. It is estimated that disulfoton production is responsible for generating approximately 300 lbs/day of wastewater treatment sludges. The sludge is expected to contain the toxic constituents toluene and o,o,o triethyl ester of phosphorodithioate.
2. It is estimated that 120 metric tons/yr of still bottoms containing o,o,o-triesters of phosphorodithioic acid and toluene are generated from the production of disulfoton.\*

\*The Agency is aware that these wastes also contain the toxic organic, disulfoton. However, due to the propensity of disulfoton to rapidly hydrolyze, it will not persist in the waste for extended periods of time. Based on this fact, the Agency will not presently regulate these wastes on the basis of disulfoton contamination.

3. Disposal of these wastes, even in drums, in improperly designed or operated landfills represents a potential hazard due to the migratory potential of these hazardous compounds.

## II. SOURCES OF THE WASTE AND TYPICAL DISPOSAL PRACTICES

### A. Profile of the Industry

Disulfoton is produced in this country by only one manufacturer, Mobay Chemical Corporation, at its Chemagro Agricultural Division in Kansas City, Missouri.<sup>(1)</sup> Production for 1974 was estimated at 10 million pounds.<sup>(2)</sup>

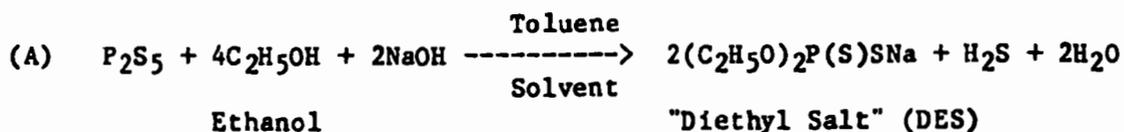
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★.

Disulfoton is a systemic insecticide, primarily used to control sucking insects, especially aphids and plant-feeding mites. It was developed in the 1950's and has been in commercial use for about 15 years. Agricultural uses accounted for almost all of the estimated U.S. consumption in 1972. Small quantities are used on ornamentals in the home and garden market in the form of dry granules of very low active ingredient content.<sup>(3)</sup>

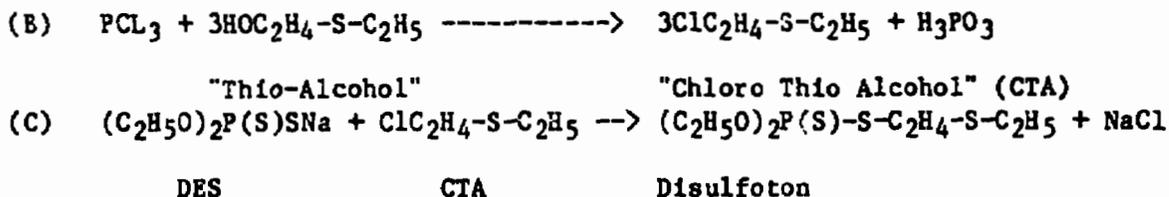
### B. Manufacturing Process

Disulfoton is produced according to the following three-step scheme<sup>(4)</sup>:



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\* The underlined data are those obtained from proprietary reports and data files.



A process flow diagram and waste schematic is shown in Figure 1. The reaction between P<sub>2</sub>S<sub>5</sub> and ethanol in toluene solvent occurs and produces the diethyl phosphorodithioic acid. The major side product of the reaction is the o,o,o-triethylester of the phosphorodithioic acid\*. The dithioic acid is next converted on the diethyl salt (DES) with caustic soda. These two substeps are summarized in reaction (A) (see equation on page 2 and corresponding (A) in Figure 1).

The DES is separated in the toluene recovery unit while the remaining mixture of toluene, triester, and other organic residues is sent to a toluene recovery unit. The toluene is recycled to the salt production process and the still bottoms (Waste Stream II in Figure 1) containing o,o,o-triethyl ester of phosphorodithioic acid go to disposal.

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PCl<sub>3</sub> and thio alcohol are then reacted to form the chloroethyl thioethyl ester ("chloroethyl thioethyl alcohol, CTA") and phosphorous acid (Reaction B, above, and corresponding (B) in Figure 1).

The third step of the production process, reaction C above, involves the reaction between the diethyl salt (DES) and chlorothio-alcohol (CTA) to form disulfoton and sodium chloride. This is shown in Figure 1 as the disyston unit, and marked (C).

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\*Also referred to in this document as o,o,o-triester.



Treatment of waste water from the manufacturing process results in a sludge (Waste Stream I in Figure 1).

C. Waste Generation and Management

As indicated in Figure 1, the diethyl salt from the DES unit is separated for further processing and the toluene, triester and other waste solids are sent to a toluene recovery unit. The recovered toluene is recycled back to the production process; the waste stream from this process (Stream II, Figure 1) is composed of the unrecovered toluene, o,o,o-triester of phosphorodithioic acid and associated organic residues. This waste is combined with waste solids from the downstream disyston recovery unit and sent for burial in landfills.(8)

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The disyston unit process water, along with wastewater from the toluene recovery unit, is sent to the disyston solvent recovery unit where some disulfoton is recovered and recycled to the disyston unit.

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The sludge from wastewater treatment (Waste Stream I in Figure 1) is disposed of by landfill; \_\_\_\_\_

(11)

\*/ The waste stream from the disyston recovery unit is not specifically listed as hazardous, but the combined waste stream is deemed hazardous under the 'mixing' provision of §261.3.

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### III. DISCUSSION OF BASIS FOR LISTING

#### A. Hazards Posed by the Wastes

There are two solid waste streams which are considered in this document. As previously mentioned, both waste streams contain toxic constituents which pose a potential hazard if improperly managed and disposed.

The still bottoms from the toluene recovery unit (Waste Stream II) are expected to contain triesters and unreacted toluene. There is little information on the toxicity of the triesters; however, the compound is structurally similar to o,o,s-triethylester, a member of a family of compound which is very toxic (LD<sub>50</sub> = 80 mg/kg after 8 days)(22). Toluene is a toxic chemical with such acute toxic effects in humans exposed to low concentrations (200 ppm) as excessive depression of the nervous system.(16)

The wastewater treatment sludges (Waste Stream I) also contain toluene solvent and o,o,o-triethylester of phosphorodithioic acid, which is a process intermediary. (For information on the toxic effects of these compounds, see Section III B.)

#### 1. Exposure Pathways

As noted above, the typical disposal method for both of these wastes is in landfills. Disposal of these wastes in landfills, even if

plastic lined drums are used, represents a potential hazard if the landfill is improperly designed or operated (the drums corrode in the presence of even small amounts of water). This can result in leaching of hazardous compounds and subsequent contamination of ground water.

As a result, the waste constituents of concern may migrate from improperly designed and managed landfills and contaminate ground and surface waters. Toluene is highly soluble (470 ppm)<sup>(24)</sup> and by virtue of its solvent properties, can facilitate mobility and dispersion of other toxic constituents assisting their movement toward ground and surface waters. The migratory potential of toluene is confirmed by the fact that toluene has been detected migrating from the Love Canal site into surrounding residential basements and solid surfaces, demonstrating ability to migrate through soils ("Love Canal Public Health Bomb", A Special Report to the Government and Legislature, New York State Department of Health (1978)). Thus, once toluene migrates from the matrix of the waste, it is likely to persist in soil and groundwater. There also may be a danger of toluene migration and exposure via an air inhalation pathway if disposal sites lack adequate cover. Toluene is relatively volatile (28.4 mm Hg (24)) and is mobile and persistent in air, having been found in school and basement air at Love Canal ("Love Canal Public Health Bomb", supra).

Although very little information is available on the characteristics of o,o,o-triethylsters, the Agency is aware of the hazardous characteristics of the same family of compounds as this particular triester. The Agency

would require some assurance that the waste components will not migrate and persist to warrant a decision not to list the waste. No such assurance appears readily available.

Thus, these waste constituents could leach into groundwater if landfills are unlined, or have inadequate leachate collection systems. Waste management facilities located in areas with highly permeable soils would likewise facilitate leachate migration.

There also may be a danger of toluene migration and exposure via an air inhalation pathway if disposal sites lack adequate cover. Toluene is relatively volatile (28.4 mm Hg (24)) and is mobile and persistent in air, having been found in school and basement air at Love Canal ("Love Canal Public Health Bomb," supra).

B. Health and Ecological Effects

1. Toluene

Health Effects - Toluene is a toxic chemical absorbed into the body by inhalation, ingestion, and through the skin. The acute toxic effect in humans is excessive depression of the central nervous system,<sup>(15)</sup> and this occurs at low concentrations [200 ppm].<sup>(16)</sup> Chronic occupational exposure to toluene has led to the development of neuro-muscular disorders.

Since toluene is metabolized in the body by a protective enzyme system which is also involved in the elimination of other toxins, it appears that over-loading the metabolic pathways with toluene will greatly reduce the clearance of other, more toxic chemicals. Additionally, the high affinity of toluene for fatty tissue can assist in the absorption of other

toxic chemicals into the body. Thus, synergistic effects of toluene on the toxicities of other contaminants may render the wastes more hazardous. Toluene is designated as a priority pollutant under Section 307(a) of the CWA. Additional information and specific references on the adverse effects of toluene can be found in Appendix A.

Ecological Effects - Toluene has been shown to be acutely toxic to freshwater fish and to marine fish. Chronic toxicity is also reported for marine fish.(18)

Regulations - Toluene has an OSHA standard for air TWA of 200 ppm. The Department of Transportation requires a "flammable liquid" label.

Industrial Recognition of Hazard - Toluene is listed as having a moderate toxic hazard rating via oral and inhalation routes (Sax, Dangerous Properties of Industrial Materials).

## 2. Phosphorodithioic and Phosphorothioic Acid Esters (Triesters)

Health Effects - The *-s,s*-methylene *o,o,o,o*-tetraethyl ester is extremely toxic by various routes of administration to animals [oral rat LD<sub>50</sub> = 13 mg/kg].(19) Toxic effects in the blood of humans have been observed at minute doses [100 micrograms/kg],(20) while human death from ingestion of this chemical has also occurred at low doses [50 mg/kg].(21) The phosphorothioic acid *-o,o,o*-triethylester is a member of a family of compounds, which, when given orally to rats is very toxic [LD<sub>50</sub> = 80 mg/kg after 8 days].(22) The *-o,o,s*-trimethyl ester is extremely toxic to rats [LD<sub>50</sub> = 15 mg/kg].(23) Additional information and specific references on adverse effects of phosphorodithioic and phosphorothioic

acid esters can be found in Appendix A.

Industrial Recognition of Hazard - Sax (Dangerous Properties of Industrial Materials), lists triethyl phosphorothioate (phosphorothioic acid, o,o,o-triethyl ester) as being highly toxic via ingestion and inhalation.

IV. References

1. Stanford Research Institute. 1977 Directory of chemical producers. SRI International, Menlo Park, California. 1977.
2. Kelso, G. L., R. Wilkenson, T. L. Ferguson, and J. R. Maloney. Development of information on pesticides manufacturing for source assessment, Final Report. Midwest Research Institute. EPA Contract No. 6B-02-1324. NTIS PB No. 283 051/1BE. July 30, 1976.
3. Von Rumker, et al. Production, distribution, use and environmental impact potential of selected pesticides. U.S. EPA, Office of Pesticide Programs. EPA No. 540/1-74-001. NTIS PB No. 238 795. 1975.
4. U.S. EPA. Lawless, E. W., R. Von Rumker, T. L. Ferguson. The pollution potential in pesticide manufacturing. TS-00-72-04. NTIS PB No. 213 782/3BA. June, 1972.
5. Not used in text.
6. Not used in text.
7. Not used in text.
8. Parsons, T., ed. Industrial process profiles for environmental use: Chapter 8, Pesticide industry. EPA No. 600/77-023h. Technology Series. NTIS PB No. 266 225. 1977.
9. Not used in text.
10. Not used in text.
11. Proprietary information submitted to EPA by Mobay Chemical Corporation through 1978 response to "308" letter.
12. Not used in text.
13. Not used in text.
14. Not used in text.
15. U.S. EPA. Toluene ambient water quality criteria. NTIS PB No. 296 805. 1979.

IV. References (Continued)

16. NIOSH. Registry of toxic effects of chemical substances. Toluene. U.S. Government Printing Office. Washington, D.C. 1978.
17. Not used in text.
18. U.S. EPA. Toluene: Hazard profile. Environmental Criteria and Assessment Office, U.S. EPA. Cincinnati, Ohio. 1979.
19. Pharmaceutical Journal 185:361. 1960.
20. Toxicol. Appl. Pharmacol. 22:286. 1972.
21. Gleason, M.N., et al. Clinical toxicology of commercial products. Acute poisoning, 3rd ed. p. 65. 1969.
22. Mallipute, et al. J. Agric. Food Chem. 27:463-466. 1979.
23. Fukuto, et al. EPA Grant No. R804345-04. Quarterly progress reports to EPA, August 1978 November, 1979.
24. U.S. EPA. Physical chemical properties of hazardous waste constituents. Prepared by Southeast Environmental Research Laboratory; Jim Falco, Project Officer. 1980.

(ORD D-1)

## LISTING BACKGROUND DOCUMENT

## PHORATE PRODUCTION

Wastewater Treatment Sludges from the Production of Phorate (T)

Filter Cake from the Filtration of Diethylphosphorodithioic Acid  
in the Production of Phorate (T)

Wastewater from the Washing and Stripping of Phorate Production (T)

I. Summary of Basis for Listing

The hazardous wastes from phorate production are: (1) wastewater treatment sludges from the production of phorate, (2) filter cake from the filtration of diethylphosphorodithioic acid, and (3) wastewater from the washing and stripping of phorate product.

The Administrator has determined that these solid wastes from phorate production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- 1) Wastes from the production of phorate may contain phorate, formaldehyde, esters of phosphorodithioic acid and phosphorothioic acid.
- 2) Phorate is extremely toxic and formaldehyde has been evaluated by the Agency as exhibiting substantial evidence of carcinogenicity. The other constituents expected to be present in the waste are also toxic.
- 3) Disposal of these wastes in improperly designed or operated landfills presents a potential hazard due to the risk of these hazardous compounds leaching into groundwater. As

these hazardous compounds are likely to persist in ground-water, drinking water supplies derived from these sources are likely to be contaminated.

- 5) Mismanagement of incineration operations could result in the release of hazardous vapors to the atmosphere and present a significant opportunity for exposure of humans, wildlife and vegetation in the vicinity of these operations to potentially harmful substances.

## II. Sources of the Wastes and Typical Disposal Practices

### A. Profile of the Industry

The principal use of phorate is as a soil and systemic insecticide used to control a wide range of insects on a variety of crops: alfalfa, barley, beans, corn, cotton, hops, lettuce, peanuts, potatoes, rice, sorghum, sugar, beets, sugar cane, tomatoes and wheat<sup>(3)</sup>.

Phorate is produced in this country by two manufacturers, American Cyanamid at Hannibal, MO<sup>(1,6)</sup> and Mobay Chemical in Kansas City, MO.\*

### B. Manufacturing Process

A generalized production and waste schematic for phorate is shown in Figure 1. Phorate is made by the reaction of o,o-diethyl hydrogen phosphorodithioate with formaldehyde, followed by the addition of ethyl mercaptan (ethanethiol). The o,o-diethyl hydrogen phosphorodithioate is condensed with formaldehyde and ethyl mercaptan. The reaction chemistry is as follows<sup>(4)</sup>:

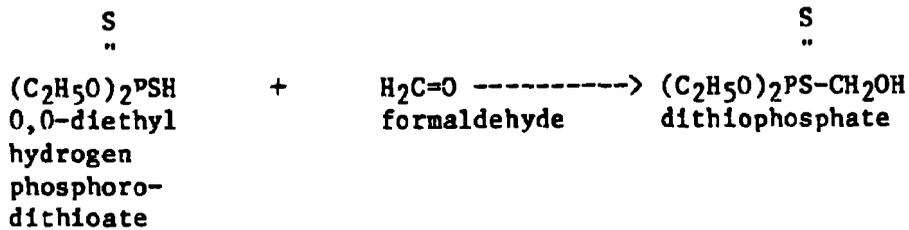
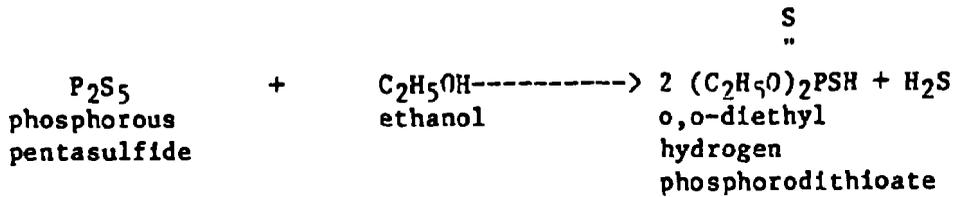
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<sup>(2)</sup> The Agency has been informed, however, that American Cyanamid no longer produces phorate.

All underlined information is from proprietary reports and data.

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- 586 - 586



These reactions indicate the source of the waste constituents of concern.

C. Waste Generation and Management

Based on the generalized flow diagram shown in Figure 1, three hazardous waste streams from the production of phorate are expected to be generated. (See figure 1.) These are:

- (a) Process wastewater: The wastewater is likely to contain significant concentrations of phorate, and lesser concentrations of other process waste constituents including formaldehyde, phosphorodithioc and phosphorothioc acid esters, and other main reaction byproducts. \_\_\_\_\_

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 \_\_\_\_\_ (2)  
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**Figure 1 is Confidential**

- (b) **Filter Cake:** The filter cake is expected to contain high concentrations of esters of phosphorodithioic acid and esters of phosphorothioic acid. These esters are formed immediately prior to filtration in the dithio acid unit, and filtration is intended to remove the esters from the process stream.
  
- (c) **Wastewater Treatment Sludges:** Wastewater treatment sludges result from the treatment of process waters. The sludges are expected to contain high concentrations of phorate because of its relative insolubility in water (about 50 ppm).<sup>(7)</sup> Lesser concentrations of other process constituents are also expected to be found in the sludge.

### III. Discussion of Basis for Listing

#### A. Hazards Posed by the Waste

These waste streams contain phorate, which is extremely toxic, and formaldehyde, a CAG carcinogen, and o,o,o-triethyl esters of both phosphorothioic acid and phosphorodithioic acid (as well as other triethyl esters which may be present), which are toxic. The presence of phorate and formaldehyde in particular, even in small concentrations, is of considerable regulatory concern, and the Administrator would require strong assurance that these waste constituents are incapable of migration, mobility, and persistence if improperly managed, before determining not to list these wastes as hazardous.

Such assurance is not forthcoming. Of the constituents likely to be found in the waste stream, phorate, o,o,o-triethyl esters of both phosphorothioic acid, and formaldehyde are able to reach environmental receptors upon release, and can persist. Phorate is moderately soluble (50 ppm), could be transported through permeable soil, and, although subject to some hydrol-

yzation and biodegradation, will persist for weeks in both surface waters and groundwater<sup>(38)</sup>. o,o,o,-Triethyl esters of phosphorothioic acid are soluble and persist in both surface water and groundwaters.<sup>(38)</sup> Formaldehyde is quite soluble and has great migratory potential.<sup>(38)</sup> If disposed of in areas with inorganic or permeable soils, it could become highly mobile. Formaldehyde also persists in surface and groundwaters<sup>(38)</sup>. Based upon estimates of EPA,<sup>(7)</sup> exposure to these compounds is likely via drinking water supplies derived from groundwater sources within areas adjacent to mismanaged land disposal sites. The projected widespread movement of these compounds when discharged to surface waters will also probably result in exposure of aquatic life forms in rivers, ponds, and lakes. Another waste constituent, o,o-diethyl ester of phosphorodithioic acid, is less persistent than the previously discussed compounds, but sufficiently soluble and resistant to degradation to result in widespread movement<sup>(7)</sup>. Thus, if improperly managed, these constituents are fully capable of migration, mobility, and persistence in substantial concentrations.

As the subject waste streams contain extremely hazardous constituents which may be mobile and persistent upon release, disposal of these wastes in landfills can create a potential hazard if landfills are improperly designed or operated. Disposal of these wastes in lagoons or treatment of wastes in holding ponds prior to final disposal, also presents substantial potential hazards as well. Unless lagoons are properly designed and operated (e.g., by lining the site with appropriate liners and employing leachate collection systems), a strong potential exists for contamination of soil and groundwaters via leachate percolation. Heavy precipitation

may result in flooding of the lagoon, thus, surface waters can become contaminated.

In light of the hazards associated with these waste constituents, and their potential for mobility and persistence in substantial concentrations if mismanaged, the wastes are deemed to be hazardous.

## B. Health and Ecological Effects

### 1. Phorate

Health Effects - Phorate is extremely toxic in animals by all routes of administration [oral rate LD<sub>50</sub> = 1.1 mg/kg].<sup>(11)</sup> Death in humans has been reported as a result of ingestion of extremely small doses. <sup>(12)</sup> Inhalation of phorate by mice caused adverse effects on reproductive performance at very low concentrations (3.0 ppm), <sup>(13)</sup> while the lethal dose by inhalation in rats is also very low [11 mg/kg].<sup>(14)</sup> Phorate metabolites are at least twice as toxic as phorate.<sup>(11,17)</sup> Additional information and specific references on adverse effects of phorate can be found in Appendix A.

Industrial Recognition of Hazard - Sax (Dangerous Properties of Industrial Materials) lists the toxic hazard rating of phorate as very high via oral and dermal routes.

### 2. Formaldehyde

Health Effects - Formaldehyde is reportedly carcinogenic<sup>(18)</sup> with

nasal cavity tumors detected in two studies. It has also been mutagenic in several bacterial and human cell culture assays.(19,22) Formaldehyde is very toxic to animals by all routes of administration (23,27), causing death in humans in small amounts (36 mg/kg).(28) Additional information and specific references on adverse effects of formaldehyde can be found in Appendix A.

Ecological Effects - Formalin, an aqueous solution of formaldehyde is lethal to Daphnia Magna.(30)

Regulatory Recognition of Hazard - Formaldehyde is a chemical evaluated by CAG as having substantial evidence of carcinogenicity.(39) OSHA has set a standard air TWA limit of 3 ppm for formaldehyde.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, lists formaldehyde as highly toxic to skin, eyes, and mucous membranes.

### 3. Phosphorodithioic and Phosphorothioic Acid Esters

Health Effects - The phosphorodithioic acid s,s'-methylene-o,o,o',o'-tetraethyl ester is extremely toxic by various routes of administration to animals [oral rat LD<sub>50</sub> = 13 mg/kg].(33) Toxic effects in the blood of humans have been observed at minute doses (100 ug/kg)(34), while human death from ingestion of this chemical has also occurred at low doses [50 mg/kg].(35)

The phosphorothioic acid o,o,o-triethyl ester is similar to the

o,o,s-triethyl ester, which is very toxic when given orally to rats [LD<sub>50</sub> = 80 mg/kg].<sup>(36)</sup> The o,o,s-triethyl ester is extremely toxic to rats [LD<sub>50</sub> = 15 mg/kg].<sup>(37)</sup> Additional information and specific references on the adverse effects of phosphorodithioic and phosphorothioic acid esters can be found in Appendix A.

Industrial Recognition of Hazards - Sax, Dangerous Properties of Industrial Materials, lists triethyl phosphorothioate (phosphorothioic acid, o,o,o-triethyl ester) as being highly toxic via ingestion, inhalation and skin absorption.

IV. References

1. SRI. 1977 Directory of chemical producers. Stanford Research Institute, Menlo Park, California. 1977.
2. Proprietary information submitted to EPA by American Cyanamid through 1978 response to "308" letter.
3. Farm Chemicals Handbook. Meister Publishing Company, Willoughby, Ohio. 1977.
4. Lawless, E. W., et al. The pollution potential in pesticide manufacturing. U.S. EPA, Office of Water Programs, Technical Studies Report TS-00-72-04. NTIS PB No. 213 782/3BA. 1972.
5. Not used in text.
6. Personal Communication. S. R. Hathaway of American Cyanamid, to D. K. Oestreich. February 11, 1980.
7. U.S. EPA. Aquatic fate and transport estimates for hazardous chemical exposure assessments. U.S. EPA, Environmental Research Laboratory, Athens, GA. February, 1980.
8. Not used in text.
9. Not used in text.
10. Not used in text.
11. National Academy of Sciences, National Research Council. Drinking water and health. PB No. 2619. 1977.
12. Gleason, M. N., et al. Clinical toxicology of commercial products: Acute poisoning, 3rd ed., p. 142. 1969.
13. U.S. EPA. M. Greenberg. Hazard profile on phorate. U.S. EPA, Environmental Criteria and Assessment Office, Research Triangle Park, NC. 1980.
14. Newell, G.W., and J.V. Dilley. Teratology and acute toxicology of selected chemical pesticides administered by inhalation. NTIS PB No. 277 077. 1978.
15. Not used in text.
16. Not used in text.

17. Curry, A.N., et al. Determination of residue of phorate and its insecticidally active metabolites by cholinesterase inhibition. Jour. Agric. Food Chem. 9:469-477. 1961.
18. U.S. EPA. The Carcinogen Assessment Group's preliminary risk assessment on formaldehyde. Type I - Air Programs. U.S. EPA, Office of Research and Development, 401 M St., S.W. Washington, D.C. 20460. 1979.
19. Auerbach, C., M. Moutschen-Dahen, and J. Mouytschen. Genetic and cytogenetic effects of formaldehyde and related compounds. Mutat. Res. 39:317-361. 1977.
20. U.S. EPA. Investigation of selected potential environmental contaminants: Formaldehyde. EPA No. 560/2-76-009. NTIS PB No. 256 839/2BA. 1976.
21. Wilkins, R.J., and H.D. MacLeod. Formaldehyde-induced DNA protein crosslinks in E. coli. Mutat. Res. 36:110-16. 1976.
22. Obe, G., and B. Beck. Mutagenic activity of aldehydes. Drug Alcohol Depend. 4:91-4. 1979.
23. Union Carbide. Toxicology studies: formaldehyde. Industrial Medicine and Toxicology Department, Union Carbide Corporation. April, 1967.
24. J. Ind. Hyg. Toxicol. 23:259. 1941.
25. ACTA Pharmalogica et Toxicologica. 6:299. 1950.
26. J. Ind. Hyg. Toxicol. 31:343. 1949.
27. Horton, A.W., R. Tye, and K.L. Stemmer. Experimental carcinogenesis of the lung. Inhalation of gaseous formaldehyde on an aerosol tar by C3H mice. J. Natl. Cancer Inst. 30 (1):30. 1963.
28. Lefaux, R. Practical toxicology of plastics. Chemical Rubber Company, Cleveland, Ohio. p. 328. 1968.
29. Not used in text.
30. Dowden, B.F., and M.J. Barrett. Toxicity of selected chemicals to certain animals. Jour. Water Pollut. Control Fed. 3:1308. 1965.
31. Not used in text.
32. Not used in text.
33. Pharmaceutical Journal. 185:361. 1960.
34. Toxicol. Appl. Pharmacol. 22:286. 1972

35. Gleason, M.N., et al. Clinical toxicology of commercial products: Acute poisoning. 3rd ed., p. 65. 1969.
36. Mallipute, et al. J. Agric. Food Chem. 27:463-466. 1979.
37. Fukuto, et al. Quarterly progress reports to EPA, August 1978--Nov., 1979. EPA Grant No. R804345-04.
38. Dawson, English, Petty. Physical chemical properties of hazardous waste constituents. 1980.
39. U.S. EPA. List of Carcinogens. Carcinogen Assessment Group (CAG), Office of Research and Development, U.S. EPA, 401 M St., S.W., Washington, D.C. 20460. April 22, 1980.

LISTING BACKGROUND DOCUMENT

TOXAPHENE PRODUCTION

Wastewater Treatment Sludge from the Production of Toxaphene (T)

Untreated Process Wastewater from the Production of Toxaphene (T)

I. Summary of Basis for Listing

The production of toxaphene, a chlorinated hydrocarbon pesticide, results in the generation of process wastewater containing heavily diluted concentrations of toxaphene, and wastewater treatment sludges that contain approximately one percent of toxaphene by weight.

The Administrator has determined that process wastewater and wastewater treatment sludge from toxaphene production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- 1) Toxaphene is present in each of these waste streams; in the case of the wastewater treatment sludge, if it is found in very high concentrations. Toxaphene has been reported to cause cancer in laboratory animals and is extremely toxic. Toxaphene has also been recognized by the Agency as exhibiting substantial evidence of being carcinogenic. It has also been shown to be mutagenic.
- 2) Approximately 7 tons of wastewater treatment sludge containing about 140 lbs. of toxaphene are generated per production day. About 19,000 tons of sludge are already disposed of in a landfill in Georgia. (5)

- 3) Disposal or treatment of these wastes in improperly designed or operated landfills or unlined lagoons could result in substantial hazard if toxaphene migrates via groundwater or surface water exposure pathways.
- 4) Toxaphene is highly persistent in the environment and bioaccumulates greatly in environmental receptors.

## II. Sources of the Waste and Typical Disposal Practices

### A. Profile of the Industry

Toxaphene is produced in this country by two manufacturers: Hercules, Inc. at its Brunswick, Georgia plant, and Vertac Chemical Company at its Vicksburg, Mississippi plant.<sup>(1)</sup> \_\_\_\_\_

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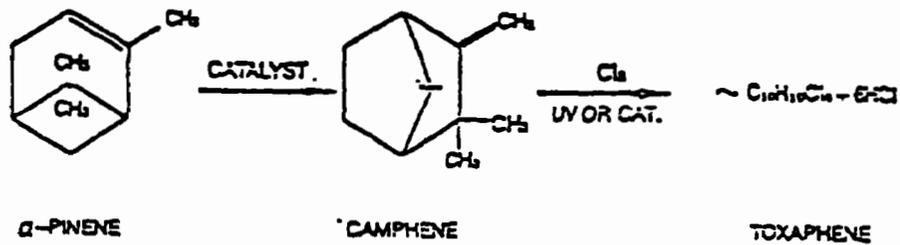
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Toxaphene is a complex mixture of polychlorinated camphenes containing 67 to 69 percent chlorine and has the approximate composition of  $C_{10}H_{10}Cl_8$ . It has been used exclusively as a non-systemic and persistent contact and ingestion insecticide. Toxaphene is marketed as a 90 percent toxaphene-10 percent solvent solution using mixed or modified xylene as the solvent. This solution is then formulated by various companies into emulsifiable concentrates, either alone or with other insecticides. Little or no toxaphene is currently being used in dust, wettable powder, or granule formulations.

\*All underlined data are obtained from proprietary reports and data.

**B. Manufacturing Process**

Toxaphene is produced in essentially the same manner by both domestic manufacturers. The reaction chemistry is as follows:(19)



**C. Waste Generation and Management\***

At the Hercules plant, wastewater is generated from the toxaphene production process (leaks, spills and washdowns), as well as from the scrubbing of vent gases in the HCl absorption and recovery step (see Figure 1).

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(2)

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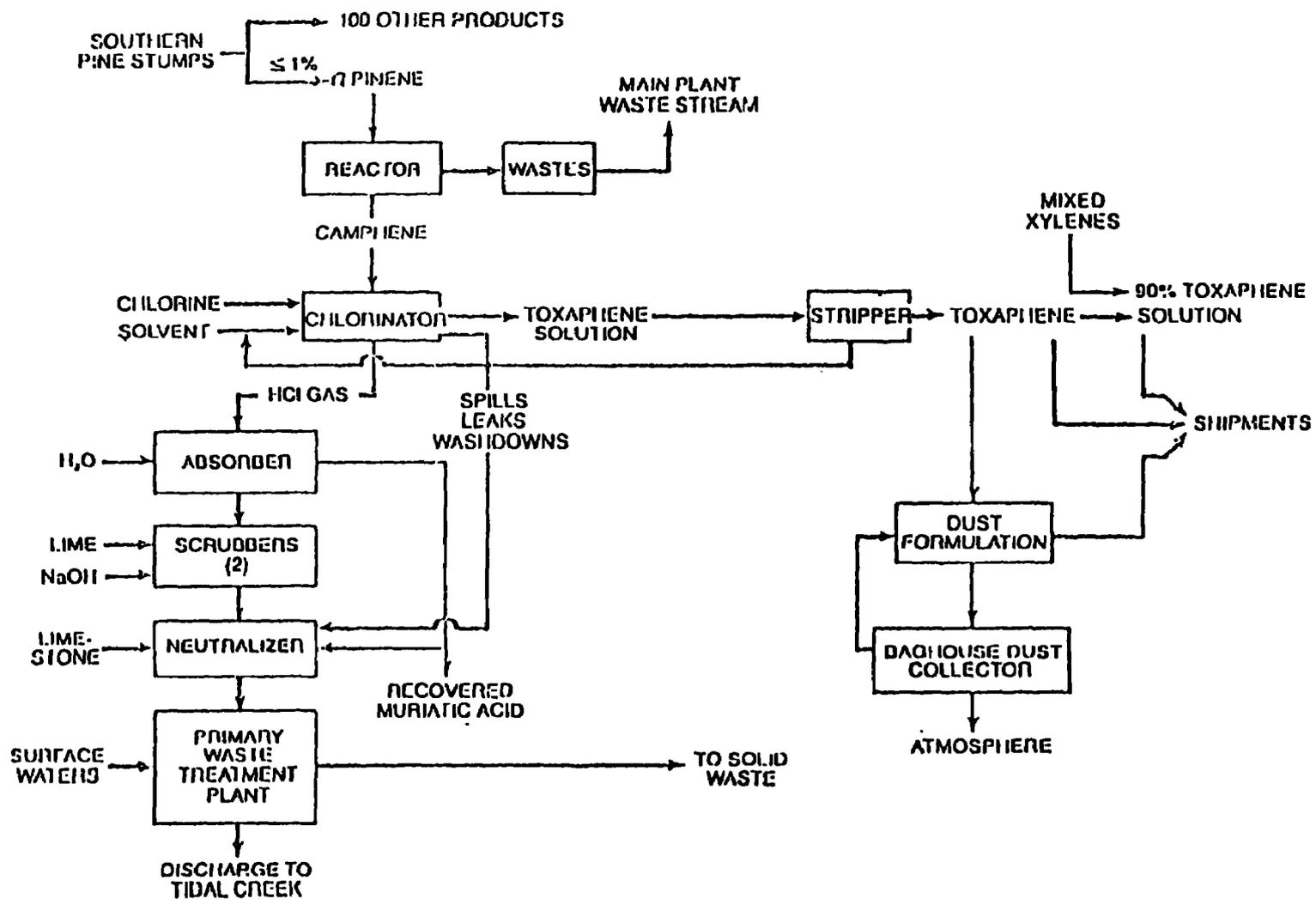
(3)

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\_\_\_\_\_ (2) The treated wastewater is directly discharged to a navigable waterway.

In Hercules' toxaphene wastewater treatment system, an average of 7 tons/day of wastewater treatment sludge (settled solids) is generated.(4,5)\* The sludge results from the addition of diatomaceous earths

\*Variations in wastewater treatment systems or in wastewater sources at the two plants may result in different concentrations of toxaphene in the wastewater treatment sludges.



- 007 -

Figure 1. HERCULES' PRODUCTION AND WASTE SCHEMATIC FOR TOXAPIENE (4)

and lime to the wastewater as sorption agents for the removal of toxaphene from the wastewater.(5) The solids are allowed to settle in holding ponds and may remain there for months at a time.(13) After the basin is filled with solids it is taken off line and the sludge is allowed to dry to approximately 50% solids.(5) Analyses of the sludge performed by Hercules indicate that the sludge contains approximately one percent toxaphene by weight, or 10,000 mg toxaphene/kg of sludge.(5) Some 140 lb/day of toxaphene are generated and will be contained in this waste stream.(4,5)

The ultimate destination of the toxaphene wastewater treatment sludge generated at the Hercules plant is a state-approved landfill.(6) The landfill is known as the "009" landfill and is a privately owned site operating under Georgia permit. It is used exclusively for the disposal of the toxaphene wastewater treatment sludge generated at the Hercules Plant.(6) The "009" landfill used for disposal of the Hercules toxaphene wastewater treatment sludge has a bentonite clay liner, and has 6 monitoring wells which are monitored 4 times per year. To date, no toxaphene has been detected in the wells.(6)

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(3).

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(5)

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(3,5)

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(3)

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\_\_\_\_\_\* This pond, or lagoon, is unlined.<sup>(14)</sup> The treated wastewater is discharged to the Mississippi River.

### III. Discussion of Basis for Listing

#### A. Hazards Posed by the Waste

As noted above, in the Hercules toxaphene wastewater treatment system, an average of 7 tons/day of waste sludge are generated.<sup>(4,5)</sup> The toxaphene content in the waste sludge is approximately at one percent by weight or 10,000 mg/Kg sludge. High concentrations of toxaphene are undoubtedly present in process wastewater to account for such high concentrations in the sludge.

Toxaphene is an exceptionally dangerous waste constituent. It is extremely toxic, highly bioaccumulative, and has been reported to cause cancer in laboratory animals. It has also been shown to be mutagenic. Toxaphene is regulated as a toxic pollutant under §307(a) of the Clean Water Act. After an adjudicative proceeding, a discharge concentration

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\*No data is currently available on the amount of wastewater treatment sludge (settled solids) generated at the Vertac plant. Nor is any data available on the concentrations of toxaphene in these sludges.

limitation of 1.5 ppb has been established for toxaphene discharges into navigable waters, and this discharge limitation was judicially upheld in Hercules, Inc. v. EPA, 598 F. 2d 91 (D.C. Cir 1978). (The administrative and judicial records are incorporated by reference into this listing background document.) The Agency has also established a national interim primary drinking water standard of .005 mg/l for toxaphene. (That administrative record is likewise incorporated by reference.)

The wastes are listed as toxic based on the potential for waste mismanagement and resulting environmental harm. Toxaphene is both mobile and persistent, having frequently been found in clarified and treated municipal drinking water.(18) Existing waste management methods could lead to release of waste toxaphene. Wastewaters are presently treated in holding ponds. Waste treatment sludge, if generated, is now disposed in landfills and unlined lagoons. Disposal in landfills represents a potential hazard if the landfill is improperly designed or operated. This can result in leaching of hazardous compounds and subsequent contamination of groundwater. Disposal in unlined lagoons also represents a potential hazard since the wastes may leach directly into the ground, resulting in possible groundwater contamination. Care must be taken to ensure that the lagoons and landfills used for storage or disposal of the toxaphene product wastes are properly designed and operated (e.g., lined with an appropriate thickness of impervious materials or provided with leachate collection/treatment systems) to prevent contamination of groundwater or surface water.

Prior to disposal in the "009" landfill, the Hercules plant treats these wastes in holding ponds which, if not properly designed and operated, may result in groundwater or surface water contamination. The high water table and the sandy composition of the soil at the location of the Hercules plant in Brunswick, Ga., make careful management of these wastes particularly important. (13)\*

Wastewater treatment sludge could also create a hazard if improperly managed. Although the sludges appear to be managed properly at the present time (suggesting that industry regards these wastes as hazardous), proper management of an otherwise hazardous waste does not make the waste non-hazardous.

One final reason for regulatory concern is noteworthy. Since toxaphene bioaccumulates in environmental receptors by factors of as much as 300,000<sup>(7)</sup>, if only a small amount leaches into the environment, a serious health hazard would be created. In the soil, toxaphene may persist from several months to more than 10 years (soil half-life is 11 years, Appendix B). It has also been shown to persist for up to 9 years in lakes and ponds.<sup>(7)</sup> Thus, the potential for human exposure is considerable. The potential for substantial hazard is, therefore, very high.

The need for the most careful management of toxaphene-containing substances is thus well-established. In light of the documented health and environmental hazards associated with toxaphene, and the fact that substantial hazard is caused by ingestion of extremely small (ppb) toxaphene concentrations, the Agency believes it is justified in listing this waste.

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\*It should be noted that Hercules' past effluent management practices have not always been adequate, as Hercules has conceded that its past effluent discharge "had an adverse effect upon the ecology' of local waters." (18)

B. Health and Ecological Effects

1. Toxaphene

Health Effects - Toxaphene is extremely toxic [oral rat LD<sub>50</sub> = 40 mg/kg].<sup>(8)</sup> Death in humans from ingestion of this dosage has also been reported.<sup>(9)</sup> Toxaphene is also lethal to animals by inhalation and skin absorption at dosages of 1 g/kg or less.<sup>(10)</sup>

Toxaphene is carcinogenic in rats and mice, causing a significant increase in the incidence of thyroid and liver cancers when administered in the diet.<sup>(12)</sup> A significant increase in liver cancer has been reported in mice at dietary levels of 50 ppm.<sup>(15)</sup>

Toxaphene and its subfractions have been found mutagenic in the standard bacterial assay (S. typhimurium, strain TA100).<sup>(16)</sup>

Ecological Effects - Toxaphene is extremely toxic to fish, and toxic to lower aquatic organisms, birds, and wild animals. The LC<sub>50</sub> (96-hour) of toxaphene in static bioassays is 3.5, 5.1 and 14 ng/l for bluegills, fathead minnows, and goldfish, respectively.<sup>(7)</sup> Toxaphene is also capable of producing deleterious effects in fish at levels as low as 0.39 ng/l, and bioaccumulates by factors of as much as 300,000.<sup>(7)</sup>

Regulations - Toxaphene has an OSHA standard for air, TWA at 500 mg/m<sup>3</sup> (Skin, SCP-F). Toxaphene is listed as a priority pollutant in accordance with §307(a) of the Clean Water Act of 1977. A 0.005 mg/l EPA National Interim Primary Drinking Water Standard has been established for toxaphene.

Industrial Recognition of Hazard - Toxaphene has been rated by Sax, Dangerous Properties of Industrial Materials<sup>(15)</sup> to be highly toxic through ingestion, inhalation, and skin absorption.

Additional information and specific references on adverse effects of toxaphene can be found in Appendix A.

#### IV. References

1. SRI. 1977 Directory of chemical producers. Stanford Research Institute. Menlo Park, California. 1977.
2. Proprietary information submitted by Hercules, Inc. to the U.S. Environmental Protection Agency in 1978 response to "308" letter.
3. Proprietary information submitted by Vicksburg Chemical Company to the U.S. Environmental Protection Agency in 1978 response to "308" letter.
4. Meiners, A. F., C.E. Mumma, T. L. Ferguson, and G. L. Kelso. Wastewater treatment technology documentation for toxaphene manufacture. Report prepared by the Midwest Research Institute for the U.S. Environmental Protection Agency. EPA No. 400/9-76-013. NTIS PB No. 253 676. February, 1976.
5. Telephone communication to Ms. Jennifer Kaduck, State of Georgia, Land Protection Branch, Environmental Protection Division, Department of Natural Resources, Atlanta, Georgia (404-656-2833). From Edward Monnig of TRW, Inc., on February 28, 1980.
6. Telephone communication to Ms. Jennifer Kaduck, State of Georgia, Land Protection Branch, Environmental Protection Division, Department of Natural Resources, Atlanta, Georgia, (404-656-2833). From S. Quinlivan of TRW, Inc., on February 12, 1980.
7. U.S. EPA. Criteria document for toxaphene. EPA No. 440/9-76-0k14. NTIS PB 253 677. June, 1976.
8. Special Publication of Entomological Society of America. College Park, MD. Vol. 74:1. 1974.
9. DHEW. Clinical Handbook on Economic Poisons. U.S. Dept. HEW, PHS, CDC, Atlanta, GA. NTIS PB No. 218 287. 1963.
10. Council on Pharmacy and Chemistry. Pharmacologic properties of toxaphene, a chlorinated hydrocarbon insecticide. JAMA 149:1135-1137. July 19, 1952.
11. Chernaff, N. and B.D. Carber. Fetal toxicity of toxaphene in rats and mice. Bull. Environ. Contam. Toxicol. 15:660-664. June, 1976.
12. National Cancer Institute. Guidelines for carcinogenesis bioassays in small rodents. Tec. Rep. No. 1 Publ. No. 017-042-00118-8. U.S. Government Printing Office, Washington, D.C. 20402. 1977.

IV. References (Continued)

13. Telephone Communications to Ms. Jennifer Kaduck, et al., State of Georgia, Land Protection Branch, Environmental Protection Division, Department of Natural Resources, Atlanta, Georgia, (404-656-2833). From Robert Karmen of EPA, on April 8, 1980.
14. Telephone Communication to Edward Monnig of TRW, Inc. From John King of EPA on April 8, 1980.
15. Litton Bionetics, Inc. Carcinogenic evaluation in mice. Toxaphene Final Report. LBI Project No. 20602. Kensington, MD. Submitted to Hercules, Inc., Wilmington, Del. Nov. 1978.
16. Hill, R.N. Mutagenicity testing of toxaphene. Memo dated Dec. 15, 1977, to Fred Hageman, Special Pesticide Review Division, U.S. Environmental Protection Agency, Washington, D.C. 1977.
17. Sax, N. Irving. Dangerous properties of industrial materials, 4th ed., Van Nostrand Reinhold Co., New York. 1975.
18. Hercules, Inc. v. EPA, 598 F. 2d 91, 99 (D.C. Cir. 1978).
19. Lawless, E.W. Pesticide Study Series -5- The Pollution Potential in Pesticide Manufacturing, Technical Studies Report; TS-00-72-04. U.S. GPO, Washington, D.C. 20402. 1972.

## LISTING BACKGROUND DOCUMENT

### 2,4,5-T PRODUCTION

- ° Heavy Ends or Distillation Residues from the Distillation of Tetrachlorobenzene in the Production of 2,4,5-T(T)

#### I. Summary of Basis for Listing

The hazardous waste from 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) production consists of the heavy ends or distillation residues from the distillation of tetrachlorobenzene in the first step of 2,4,5-T manufacture.

The Administrator has determined that the tetrachlorobenzene distillation heavy ends in 2,4,5-T production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. The heavy ends from distillation of tetrachlorobenzene contain several chlorinated benzenes including hexachlorobenzene and ortho-dichlorobenzene.
2. Hexachlorobenzene is a reported carcinogen. Ortho-dichlorobenzene is chronically toxic.
3. Disposal of these wastes in improperly designed or operated landfills could create a substantial hazard due to the migratory potential and environmental persistence of these hazardous compounds. Both groundwater and surface water are exposure pathways of concern.
4. Volatilization of the waste constituents from landfills, as has been documented, could result in the release of hazardous vapors to the atmosphere and present a significant opportunity for exposure of humans, wildlife, and vegetation in the vicinity of these operations to potentially harmful substances.

## II. Sources of the Waste and Typical Disposal Practices

### A. Profile of the Industry

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\*(1,5,6)†

The 2,4,5-trichlorophenol (TCP) salts and esters, including 2,4,5-T, are selective herbicides used to control woody plants, especially on range land and rights-of-way, where 2,4-D is not effective. The properties and actions of these compounds are similar to 2,4-D formulations. These compounds are used extensively in forest conifer control and for weed control, and for rice crops.(8)

### B. Manufacturing Process

Figure 1 is the process flow diagram of the manufacture of 2,4,5-T (2,4,5-trichlorophenoxyacetic Acid).(7) The first step in 2,4,5-T manufacture is the reaction of chlorobenzene with chlorine to form tetrachlorobenzene (TCB). Distillation is then used to separate the TCB from other chlorobenzenes. The waste of concern is generated at this point in the process, and consists of the distillation residues. Following this, the distilled TCB is hydrolyzed to form TCP and then esterified to form 2,4,5-T.(7)

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\*The underlined data are those obtained from proprietary reports and data files.

†Some of the companies listed above may no longer produce 2,4,5-T

-8-  
-594-  
-611-

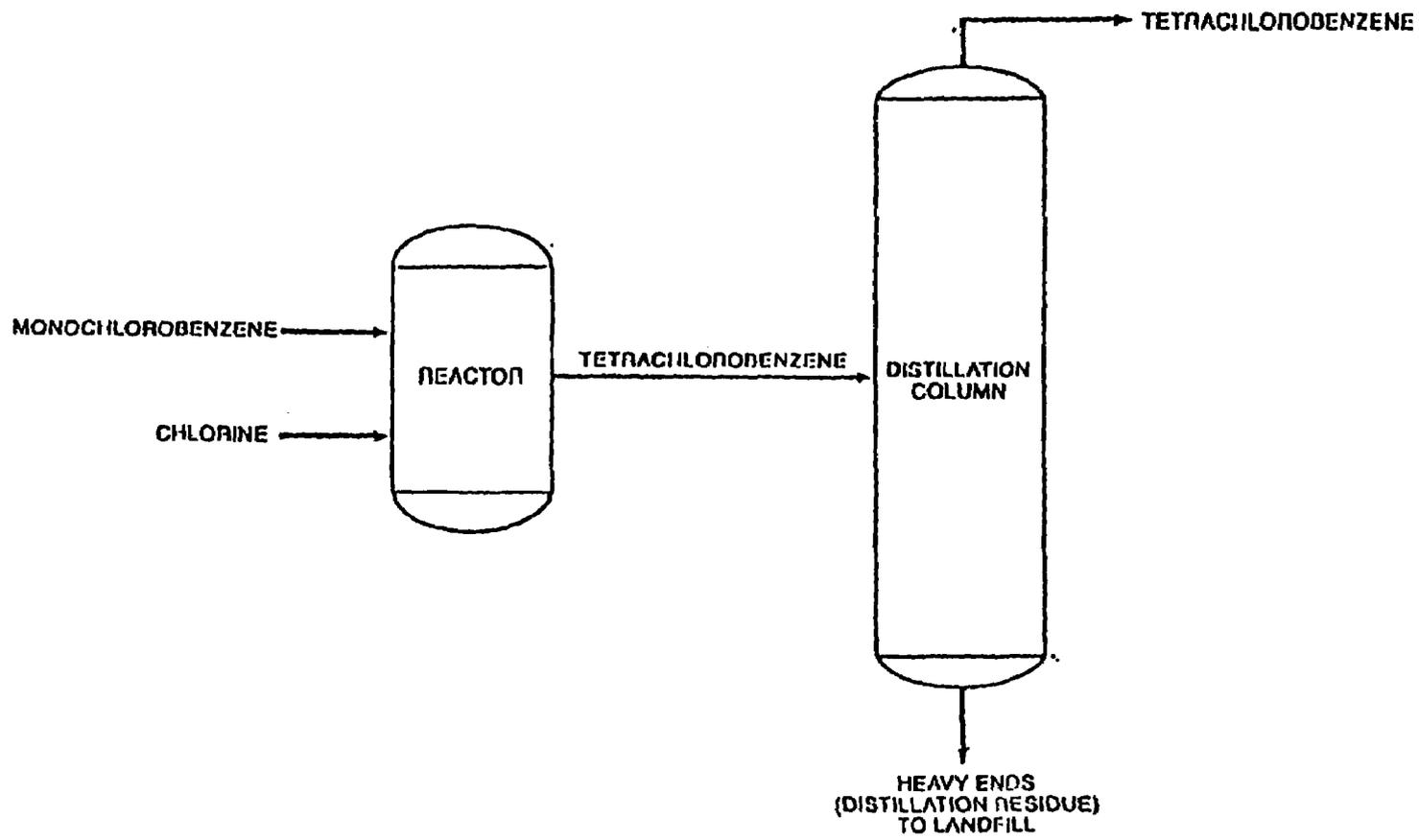


Figure 1. GENERATION OF HEAVY ENDS (DISTILLATION BOTTOMS) FROM TETRACHLOROBENZENE MANUFACTURE IN THE 2, 4, 6-T PROCESS (7)

### C. Waste Generation and Management

The heavy ends or distillation residues generated in separating TCB from other chlorobenzene make up the hazardous waste stream of concern. These residues are likely to contain all of the benzene chlorination by-products including those higher than chlorobenzene, such as ortho-dichlorobenzene and hexachlorobenzene. Further, since the waste consists largely of heavy chlorinated organic by-products, concentrations of these constituents will probably be high.

Based on current industry practice involving similar wastes, the distillation residues are probably managed by landfilling. Disposal may involve surface placement, uncontained burial, or burial in barrels in a landfill.

### III. Discussion of Basis for Listing

#### A. Hazards Posed by the Waste

The heavy ends discussed above contain hazardous compounds which can be expected to pose a serious threat to the environment if improperly managed or disposed. Among the compounds expected to be present are hexachlorobenzene and ortho-dichlorobenzene.

Hexachlorobenzene is believed to be carcinogenic and teratogenic, while o-dichlorobenzene may pose a chronic toxicity hazard via a water exposure pathway.\* To warrant a decision not to list this waste, therefore, the Administrator would require assurance that the waste constituents are incapable of migration and mobility even if improperly managed, and that these constituents will not persist if they are released into the environment.

\* It is projected that o-dichlorobenzene could create a chronic toxicity hazard if it migrated at several orders of magnitude less than

Indications are that these waste constituents are capable of migration, mobility and persistence to cause substantial hazards. The groundwater exposure pathway is of principal concern. Hexachlorobenzene, while relatively insoluble, has been detected to have migrated via a groundwater pathway from Hooker Chemical Corporation's S area, Hyde Park, and 102d St. landfills in Niagara, New York.<sup>(37)</sup> Orthodichlorobenzene is relatively soluble (App. B), and thus may be available for environmental release.

Present waste disposal practices may be inadequate to prevent waste migration. Certainly, improper management may result in release of harmful constituents. Thus, uncontained landfill burial would not impede leachate migration in areas with relatively or highly permeable soils, or where the water table is so high that groundwater acts as a leaching medium.\* Containerization in landfilled drums could still result in contaminant release, since all drums have a limited life span as the exterior metal corrodes in the presence of even small amounts of moisture. When this occurs, the potential for groundwater contamination is high if the landfill is not properly designed and operated. Improper disposal techniques in surface containment sites may also present the possibility of surface runoff contamination. A break in a pond dike or rainwater flowing over an improperly covered landfill containing the process wastes may allow migration to surface soils and surface water.

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\*Laboratory studies of the behavior of chlorinated benzenes in soil that is high in sand and low in organic content indicate that hexachlorobenzene would be likely to exhibit slow but measureable mobility in these soils again indicating that soil attenuation will not prevent environmental release of migrating contaminants.<sup>(3)</sup>

Hexachlorobenzene may also pose a substantial hazard via an air inhalation pathway if landfills are not adequately covered, as shown by a number of actual damage incidents. In May, 1976, hexachlorobenzene-containing wastes from a Vulcan plant in Louisiana volatilized and resulted in the death of cattle grazing in contaminated areas.<sup>(39)</sup> A similar case history of environmental damage in which air, soil, and vegetation over an area of 100 square miles were contaminated by hexachlorobenzene (HCB) occurred in 1972.<sup>(39)</sup> There was volatilization of HCB from landfilled wastes and subsequent bioaccumulation in cattle grazing in the eventually contaminated areas. Accumulation in tissues of cattle occurred, so the potential risk to humans from eating contaminated meat and other foodstuffs is significant.

The waste constituents of concern also can be expected to persist should they migrate from the matrix of the waste. Hexachlorobenzene is very persistent.\* (App. B) O-dichlorobenzene is subject to certain degradative processes, but would be likely to persist in groundwater. (App. B.) Hexachlorobenzene, in addition to being persistent, is very bioaccumulative, increasing its likelihood to cause harm should it migrate. (App. B)

### 3. Health and Ecological Effects

#### 1. Hexachlorobenzene

Health Effects - Hexachlorobenzene has been shown to be carcinogenic in animals<sup>(19,20)</sup> and has been identified by the Agency to be carcinogenic. This chemical is reportedly teratogenic, known

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\*Evidence of mobility and resistance to degradation has been shown by identification of chlorobenzene isomers in ground water in Florida.<sup>(36)</sup> Chlorinated benzenes are likely to persist in the environment and to bioaccumulate.<sup>(17)</sup>

to pass through placental barriers, producing toxic and lethal effects in the fetus.<sup>(21)</sup> Chronic exposure to HCB in rats has been shown to result in damage to the liver and spleen.<sup>(22)</sup> It has been lethal in humans when ingested at one-twentieth the known oral LD<sub>50</sub> dose for rats.<sup>(23)</sup> It has also been demonstrated that at doses far below those which are lethal, HCB enhances the body's capability to toxify rather than detoxify other foreign organic compounds present in the body through its metabolism.<sup>(24)</sup> Additional information and specific references on the adverse effects of hexachlorobenzene can be found in Appendix A.

Ecological Effects - Hexachlorobenzene is likely to contaminate accumulated bottom sediments within surface water systems and bioaccumulate in fish and other aquatic organisms.<sup>(18)</sup>

Regulatory Recognition of Hazard - Hexachlorobenzene is a chemical evaluated by CAG as having substantial evidence of carcinogenicity. Ocean dumping of hexachlorobenzene is prohibited. An interim food contamination tolerance of 0.5 ppm has been established by FDA.

Industrial Recognition of Hazard - According to Sax, Dangerous Properties of Industrial Chemicals, HCB is a fire hazard and, when heated, emits toxic fumes.

## 2. Ortho-dichlorobenzene

Health Effects - Ortho-dichlorobenzene is very toxic in rats [oral LD<sub>50</sub> = 500 mg/kg].<sup>(25)</sup> Human death has also occurred at this level.<sup>(26)</sup> Chronic occupational exposure to this chemical and its isomer has resulted in toxicity to the liver, central nervous system and respiratory system.<sup>(27)</sup> Chronic oral feeding of ortho-dichloro-

benzene to rats in small doses has caused anemia as well as liver damage and central nervous system depression.(28) Additional information and specific references on the adverse effects of ortho-dichlorobenzene can be found in Appendix A.

Regulatory Recognition of Hazard - Ortho-dichlorobenzene has been designated as a priority pollutant under Section 307(a) of the CWA. The OSHA standard for O-dichlorobenzene is 50 ppm for an 8 hour TWA. It has been selected by NCI for Carcinogenesis Bioassay, September, 1978.

The Office of Water and Waste Management has completed pre-regulatory assessment of O-dichlorobenzene under the Clean Water Act and the Safe Drinking Water Act. Under section 311 of the Clean Water Act, regulation has been proposed. The Office of Research and Development has begun pre-regulatory assessment of O-dichlorobenzene under the Clean Air Act.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, lists the toxic hazard ratings for O-dichlorobenzene as moderate via inhalation and oral routes.

#### IV. References

1. Proprietary information submitted to EPA by Thompson-Hayward Chemical Co. Kansas City, Kansas in 1978. Response to "308" Letter.
2. Not used in text.
3. NIOSH. Suspected carcinogens: A subfile of the NIOSH toxic substances list. U.S. HEW, PHS, CDC. Available from U.S. Government Printing Office, Washington, D.C. 20402. June, 1975.
4. Not used in text.
5. Proprietary information submitted to EPA by Dow Chemical Corporation. Midland, Michigan in 1978. Response to "308" Letter.
6. Proprietary information submitted to EPA by Transvaal, Inc. (Vertac). Jacksonville, Arkansas in 1978. Response to "308" Letter.
7. Gilbert, E. E., et al. U.S. Patent 2,830,083. April 8, 1958; Assigned to Allied Chemical Corporation. In M. Sittig, Pesticides Process Encyclopedia. Noyes Data Corporation. Park Ridge, New Jersey. 1977.
8. Farm Chemicals Handbook. Meister Publishing Company, Willoughby, Ohio. 1977.
9. Not used in text.
10. Not used in text.
11. Not used in text.
12. Not used in text.
13. Not used in text.
14. Not used in text.
15. Not used in text.
16. Not used in text.
17. IARC Monographs. Evaluation of carcinogenic risk of chemicals to man. 2,4,5- and 2,4,6-Trichlorophenol. Inter-Agency for Research on Cancer. Lyon, France. World Health Organization. Vol. 20:349. 1979.
18. U.S. EPA. Technical support document for aquatic fate and transport estimates for hazardous chemical exposure assessments. Environmental Research Lab. Athens, Ga. 1980.

19. Cabral, J. R. P., et al. Carcinogenic activity of hexachlorobenzene in hamsters. Tox. Appl. Pharmacol. 41:155. 1977.
20. Cabral, J. R. P., et al. Carcinogenesis study in mice with hexachlorobenzene. Toxicol. Appl. Pharmacol. 45:323. 1978.
21. Grant, D. L., et al. Effect of hexachlorobenzene on reproduction in the rat. Arch. Environ. Contam. Toxicol. 5:207. 1977.
22. Koss, G., et al. Studies on the toxicology of hexachlorobenzene. III. Observations in a long-term experiment. Arch. Toxicol. 40:285. 1978.
23. Gleason, M.N., et al. Clinical toxicology of commercial products - Acute poisoning. 3rd ed., p. 76. 1969.
24. Carlson, G. P. Induction of cytochrome P-450 by halogenated benzenes. Biochem. Pharmacol. 27:361. 1978.
25. Gleason, M.N., et al. Clinical toxicology of commercial products. 3rd ed., p. 49. 1969.
26. U.S. EPA. Dichlorobenzenes: Ambient water quality criteria. NTIS PB No. 292 429. 1979.
27. Varshavskaya, S. P. Comparative toxicological characteristics of chlorobenzene and dichlorobenzene (ortho- and para-isomers) in relation to the sanitary protection of water bodies. Gig. Sanit. 33:17. 1967.
28. Ben-Dyke, R., D.M. Sanderson, and D.N., Noakes. Acute toxicity for pesticides. World Rev. Pest Control 9:119-127. 1970.
29. Not used in text.
30. Not used in text.
31. Not used in text.
32. Not used in text.
33. Not used in text.
34. Not used in text.
35. Not used in text.
36. Not used in text.
37. Office of Public Health, New York State Department of Health. Love Canal-Public Health Time Bomb. September, 1978.

38. Dawson, English, and Petty. Physical chemical properties of hazardous waste constituents. 1980.
39. U.S. EPA. Open files. Hazardous Site Control Branch, WH-548, U.S. EPA, 401 M St., S.W., Washington, D.C. 20460. Contact Hugh Kaufman (202) 245-3051.
40. Not used in text.

Response to Comments - Heavy Ends or Distillation Residues from  
the Distillation of Tetrachlorobenzene in the Production of 2,4,5-T

Heavy ends or distillation residues from the distillation of tetrachlorobenzene in the production of 2,4,5-T (K042) is listed as hazardous because it contains a number of chlorinated benzenes including hexachlorobenzene and ortho-dichlorobenzene. One commenter objected to the inclusion of ortho-dichlorobenzene as a constituent of concern in this particular listing. The commenter argued that compounds with an LD<sub>50</sub> of 500 mg/kg, the oral LD<sub>50</sub> of ortho-dichlorobenzene, is considered by "toxicologists" to be only slightly or moderately toxic. The commenter, therefore, recommends that ortho-dichlorobenzene be deleted as a basis for listing waste K042.

The Agency disagrees with this unsubstantiated conclusion. A number of standard references, in evaluating acute toxicity, consider compounds with an oral LD<sub>50</sub> of 500 mg/kg to be "very toxic." For example, "Clinical Toxicology of Commercial Products", Gleason, et al., 3rd Edition, Baltimore, Williams and Wilkins, 1969, considers compounds which have an oral LD<sub>50</sub> (as determined using rats) in the range of 50 mg/kg to 500 mg/kg to be very toxic. Additionally, in the Registry of Toxic Effects, a widely used reference book which is published by the National Institute for Occupational Safety and Health (NIOSH), guidelines for evaluating acute\* dosages differentiating relatively toxic from non-toxic substances have been set; the LD<sub>50</sub>

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\*Applies to those substances for which acute or short term toxicity characterizes the response.

level indicated is 5000 mg/kg. The Agency, therefore, could continue to include ortho-dichlorobenzene as a constituent of concern in this particular listing, on the basis of acute toxicity effects alone.

Furthermore, o-dichlorobenzene is chronically toxic (see Background Document, pp. 603-04), a point ignored by the commenter. Listing of this compound as a constituent of concern is consequently further justified.

## LISTING BACKGROUND DOCUMENT

## 2,4-D PRODUCTION

2,6-Dichlorophenol waste from the Production of 2,4-D (T)

Untreated Wastewater from the Production of 2,4-D (T)

I. Summary of Basis for Listing

These wastes from 2,4-D production may contain a number of toxic constituents, including 2,4-dichlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol and chlorophenol polymers.

The Administrator has determined that the subject solid wastes from 2,4-D production may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. The wastewater generated from the production of 2,4-D contains 2,4-dichlorophenol, and 2,4,6-trichlorophenol. 2,6-Dichlorophenol waste contains substantial concentrations of 2,6-dichlorophenol, 2,4,6-trichlorophenol and 2,4-dichlorophenol.
2. 2,4,6-Trichlorophenol has been identified by EPA's Carcinogen Assessment Group as a substance which has exhibited substantial evidence of carcinogenicity. It has also been cited in the literature as being mutagenic. 2,4-Dichlorophenol and 2,6-dichlorophenol are toxic.
3. Management of these wastes in treatment lagoons or landfills creates the potential for soil or groundwater contamination via leaching if mismanagement occurs.

II. Sources of Wastes and Typical Disposal Practices

A. Profile of the Industry

2,4-D is a selective herbicide registered for use on grasses, barley, corn, oats, sorghum, wheat and non-crop areas for post-emergent control of weeds. (7)

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2. \_\_\_\_\_
3. \_\_\_\_\_

B. Manufacturing Process

In the 2,4-D manufacturing process, benzene is chlorinated to produce monochlorobenzene, which is hydrated to produce phenol. (2a) Chlorination of phenol also leads to the generation of by-product 2,6-dichlorophenol and other chlorophenols (principally 2,4,6-trichlorophenol). (2a) Figure 1 illustrates an example of this manufacturing process.

C. Waste Generation

1. Generation of 2,6-dichlorophenol waste.

Chlorination of phenol inevitably leads to the generation of by-product 2,6-dichlorophenol and other chlorophenols. (2a)

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(8,10) As shown in

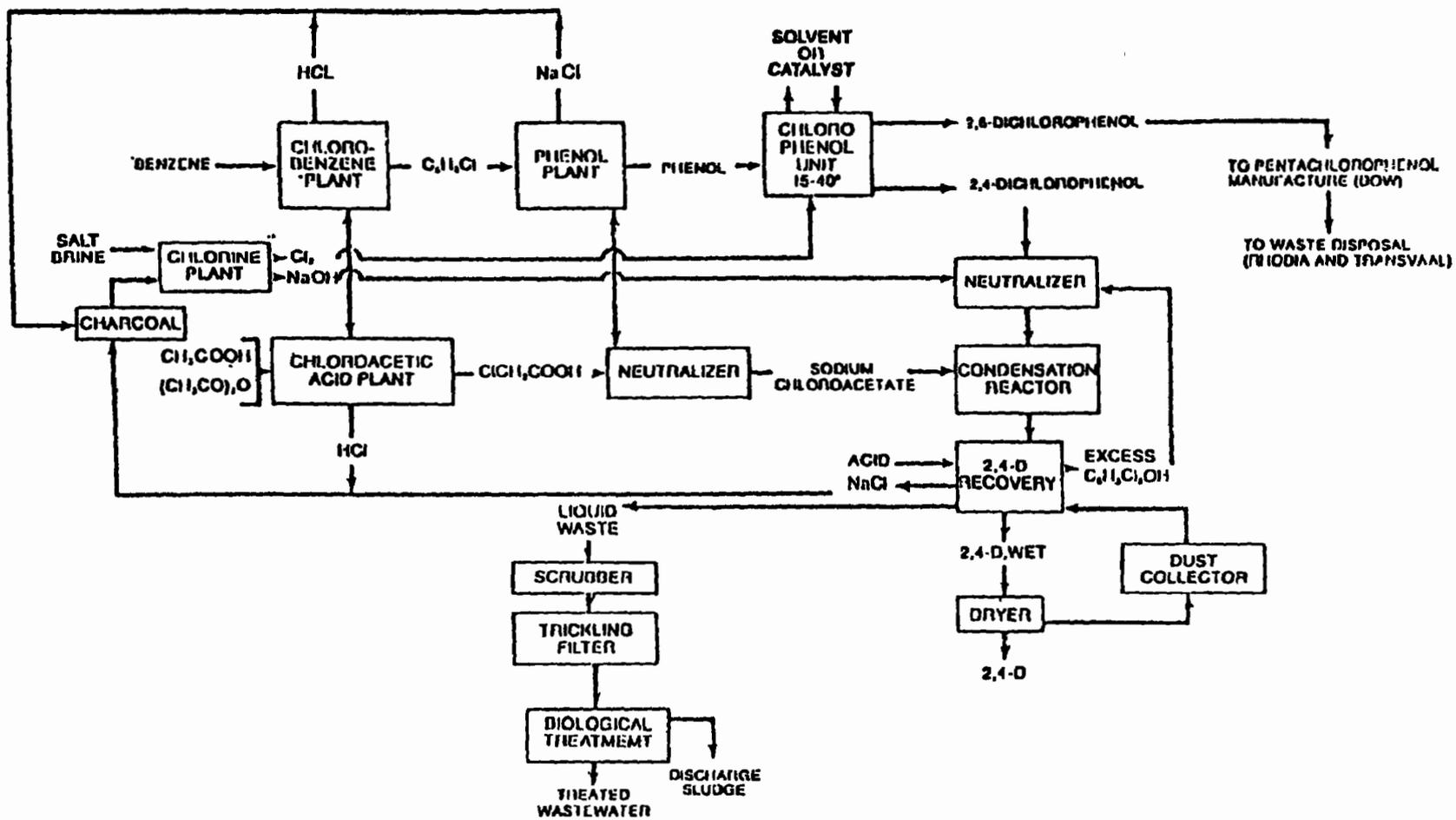


Figure 1. PRODUCTION AND WASTE SCHEMATIC FOR 2,4-D (MODIFIED FROM REFERENCE 1)

Figure 1, 2,6-dichlorophenol is taken off overhead from the chlorophenol unit as a by-product. This 2,6-dichlorophenol by-product is used in the production of pentachlorophenols in the plant, and therefore is not a waste; in two other 2,4-D plants, the 2,6-dichlorophenol by-product is disposed of as a waste,\* and is included in this listing. This waste is composed of 2,6-dichlorophenol, 2,4,6-trichlorophenol, 2,4-dichlorophenol, and chlorophenol polymers (see page 5). (8,10)

Various 2,6-Dichlorophenol generation rates have been reported. \_\_\_\_\_

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\_\_\_\_\_ (10) \_\_\_\_\_

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\_\_\_\_\_ (8)

2. Generation of wastewater.

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\*The Transvaal (Vertac) plant does not reuse 2,6-dichlorophenol as feedstock material, so it is quite likely that this plant generates 2,6-dichlorophenol waste.

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(8) Process wastewater is removed for treatment. This wastewater, prior to treatment, is listed as hazardous. 2,4-Dichlorophenol is the intermediate used in the production of 2,4-D; some of this chemical becomes entrained in the wastewater. It is expected that some quantities of 2,6-dichlorophenol are also carried forward (see Fig. 1).

D. Waste Management

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(10)

Wastewater from Dow Chemical's 2,4-D unit is first chemically treated, then passed through a trickling filter on the way to a central biological waste treatment plant.(2a) Biological treatment sludges from the production of 2,4-D at the Dow plant are limestone-treated and disposed in an on-site landfill. At the Transvaal, Inc. (Vertac) plant, wastewater goes to a neutralization ditch.

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(9)

III. Discussion of Basis for Listing

A. Hazards Posed by the Waste

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(3,11):

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(The waste constituents of concern are 2,4,6 trichlorophenol and 2,4 dichlorophenol.)\* \_\_\_\_\_

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\_\_\_\_\_ . Disposal in landfills, even if plastic lined drums are used, could create a potential hazard if the landfill is improperly designed or operated (i.e., drums corrode in the presence of even small amounts of water). This can result in leaching of hazardous compounds with resultant contamination of surface and ground waters.

A similar potential hazard exists when wastewaters from 2,4-D production are impounded in treatment lagoons. The

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\*Other waste constituents are not deemed present in sufficient concentrations to be of regulatory significance.

same hazardous constituents are present in the solids that will settle to the bottom of the lagoon. The concentrations of the hazardous constituents in the settled solids are expected to be much higher than those found in the wastewater itself, which obviously contains a much greater volume of water\*. Hazardous constituents may leach from the lagoon bottom to contaminate groundwater. In addition, possible incomplete treatment in biological treatment lagoons may allow these hazardous constituents to reach the ultimate disposal site, where the potential for leachate exposure exists.

An example of the consequences which may result when these wastes are mismanaged occurred at the Transvaal, Inc. plant, which produces 2,4-D, in Jacksonville, Arkansas. Sludge from 2,4-D manufacture is sent to a chemical landfill adjacent to the plant. Soil and groundwater near the chemical landfill have been found to be contaminated with toxic chloro-phenols from 2,4-D manufacture.\*\*

As this incident illustrates, waste constituents may well prove mobile and persistent. As to mobility, the chlorinated phenols present in the waste may undergo bio-degradation in

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\*This indicates that the dredged sludges from lagoons are not expressly listed here. These sludges are nevertheless reached by this listing; Section 261.3 of the Regulations provides that the solid wastes discharged from a hazardous waste treatment facility are also considered hazardous unless the generator demonstrates otherwise.

\*\*OSW Hazardous Waste Division, Hazardous Waste incidents, unpublished open file 1978.

soil if present in low concentrations. (25) It seems likely, however, the rates of degradation of these compounds in the soil profile would be low because of repression of soil microbial activity by these and other waste components. (Also, mismanagement could occur in areas where soil is low in organic content, so mobility in soil would not be substantially effected.) All of these compounds also are quite soluble in water [for 2,4-dichlorophenols-4,500 mg/l at 25°C and 4,600 mg/l at 20°C]<sup>28</sup> and do not exhibit a high propensity to adsorb in soils. (25) Hence, they would be expected to move readily into groundwater. The potential for movement of these compounds into and through groundwater is illustrated by a case history in California, where long-term pollution of groundwater by phenolic substances occurred because of release into the soil of water containing 2,4-dichlorophenol from 2,4-D manufacture. (26) High waste loads such as landfill dumping would inhibit degradation and therefore increase the likelihood of adverse environmental effects.

## B. Health and Ecological Effects

### 1. 2,4-Dichlorophenol/2,6-dichlorophenol

Health Effects - 2,4-Dichlorophenol has high oral toxicity [oral LD<sub>50</sub> (rats) = 580 mg/kg]. (12) In addition, this chemical promotes DMBA-initiated skin cancer in mice. (13) It is also reported to adversely affect carbohydrate metabolism. (14,15) 2,6-Dichlorophenol is also toxic in animals;

it inhibits liver mitochondrial respiration, and, at relatively high concentrations affects the nervous system.(29) Additional information and specific references on the adverse effects of 2,4- and 2,6-dichlorophenol can be found in Appendix A.

Ecological Effects - Small doses of 2,4-dichlorophenol have been lethal to fresh water fish and invertebrates.(17)

Regulatory Recognition of Hazard -

2,4-Dichlorophenol is designated as a priority pollutant under Section 307(a) of the CWA. The Office of Water and Waste Management has completed a pre-regulatory assessment and proposed water quality criteria for 2,4-dichlorophenol under sections 304(a) and 311 of the Clean Water Act. The Office of Research and Development is presently conducting a pre-regulatory assessment of 2,4-dichlorophenol under the Clean Water Act.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials, designates a toxic hazard rating of moderate toxicity for 2,4-dichlorophenol. However, chlorinated phenols are designated as highly toxic local and systemic compounds.

2. 2,4,6-Trichlorophenol

Health Effects - 2,4,6-trichlorophenol induced cancer in mice during long-term oral feeding studies.(18) This compound has also been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of

carcinogenicity.(27) It is acutely lethal to humans by ingestion at 60 percent of the oral LD50 dose in rats [500 mg/Kg] (19) and is mutagenic to yeast,(20) and adversely affects cell metabolism.(21,22) Additional information and specific references on the adverse effects of 2,4,6-trichlorophenol can be found in Appendix A.

Ecological Effects - Very small concentrations of 2,4,6-trichlorophenol are lethal to freshwater fish [LC50 = 426 ug/l]; it is also lethal to freshwater invertebrates at very low concentrations.(24)

Regulatory Recognition of Hazard - 2,4,6-Trichlorophenol has been designated as a Priority Pollutant under Section 307(a) of the CWA. Based on carcinogenicity, EPA has recommended 12 ug/l as the ambient water quality criterion for the ingestion of fish and water.(28)

Industrial Recognition of Hazard. Sax, in Dangerous Properties of Industrial Materials, lists 2,4,6-trichlorophenol as moderately toxic via the oral route.

## REFERENCES

1. U.S. EPA. Office of Water Programs. The pollution potential in pesticide manufacturing. NTIS PB No. 213 782. June, 1972.
- 2a. U.S. EPA. Office of Pesticide Programs. Production distribution, use and environmental impact potential of selected pesticides. EPA No. 540/1-74-001. NTIS PB No. 238 395/9BA. 1975.
- 2b. Aly, O.M., and S.D. Faust. Studies on the fate of 2,4-D and ester derivatives in natural surface waters. J. Agr. Food Chem. 12(6):541-546. 1964.
3. U.S. EPA. Industrial process profiles for environmental use, Chapter 8: Pesticides. EPA No. 600/77-023h. Research Triangle Park, North Carolina. NTIS PB No. 266 255/2BE. January, 1977.
4. Not used in text.
5. Not used in text.
6. Not used in text.
7. Farm Chemicals Handbook. Meister Publishing Company, Willoughby, Ohio. 1977.
8. Proprietary information submitted to EPA by Rhodia, Inc., Agri. Division. Portland, Oregon in 1978 response to "308" letter.
9. Proprietary information submitted to EPA by Transvaal, Inc. Jacksonville, Arkansas in 1978 in response to "308" letter.
10. Proprietary information submitted to EPA by Rhodia, Inc., on March 7, 1977.
11. Proprietary information from Draft Contractor Technical report for BAT Technology in the Pesticide Chemicals Industry by Environmental Science and Engineering, Inc., for U.S. EPA, 1979.
12. Deichmann, W. The toxicity of chlorophenols for rats. Fed. Proc. (Fed. Am. Soc. Exp. Biol.) 2:76. 1943.
13. Boutwell, R. K. and Bosch. The tumor-promoting action of phenol and related compounds for mouse skin. Can. Res. 19:413-424. 1959.

14. Farquharson, M.E., et al. The biological action of chlorophenols. Br. Jour. Pharmacol. 13:20. 1958.
15. Mitsuda, W., et al. Effect of chlorophenol analogues on the oxidative phosphorylation in rat liver mitochondria. Agric. Biol. Chem. 27:366. 1963.
16. Not used in text.
17. U.S. EPA. In-depth studies on health and environmental impacts of selected water pollutants. Contract No. 68-01-4646. 1978.
18. NCI. Carcinogenesis bioassay, 2,4,6-trichlorophenol. NTIS PB No. 223 159. Sept. 1978.
19. Gleason, M.N., et al. Clinical toxicology of commercial products, 3rd ed. Williams and Wilkins, Co. Baltimore. 1969.
20. Fahrig, R. et al. Genetic activity of chlorophenols and chlorophenol impurities. Pg. 325-338. In: Pentachlorophenol: chemistry, pharmacology and environmental technology. K. Rango Rao. Plenum Press, New York. 1978.
21. Weinback, E. C., and J. Garbus. The interaction of uncoupling phenols with mitochondria and with mitochondrial protein. Jour. Biol. Chem. 210:1811. 1965.
22. Mitsuda, H., et al. Effect of chlorophenol analogues on the oxidative phosphorylation in rat liver mitochondria. Agric. Biol. Chem. 27:366. 1963.
23. Not used in text.
24. Not used in text.
25. Kozak, V.P., G.V. Simmons, G. Chesters, D. Stevsby, and J. Harkins. Reviews of the environmental effects of pollutants: XI Chlorophenols. EPA No. 600/1-79-012. U.S. EPA. Washington, D.C. pp. 492. 1979.
26. Sinenson, H. A. The Montebello incident. Proc. Assoc. Water Treatment and Exam. 11:84-88. 1972.
27. U.S. EPA. Carcinogen Assessment Group, Office of Research and Development. List of Carcinogens. April 22, 1980.

- . U.S. EPA. Ambient water quality criteria for trichloro-phenols. EPA 440/5-80-032. 1980.
- 29. Chung, Y. Studies on cytochemical toxicities of chloro-phenols to rats. Yakhak Hoe Chi. 22:175. 1978.

Response to Comments - 2,6-Dichlorophenol Waste from  
the Production of 2,4-D

One commenter raised several questions with respect to waste K043 (2,6-Dichlorophenol waste from the production of 2,4-D).

1. 2,6-Dichlorophenol waste from the production of 2,4-D (K043) is listed as hazardous because it contains substantial concentrations of 2,6-dichlorophenol, 2,4,6-trichlorophenol and 2,4-dichlorophenol. The commenter objected to the inclusion of 2,4-dichlorophenol as a constituent of concern in this particular listing. The commenter argued that compounds with an LD<sub>50</sub> of 580 mg/kg, the oral LD<sub>50</sub> of 2,4-dichlorophenol, is considered by toxicologists to be only slightly or moderately toxic. The commenter, therefore, recommends that 2,4-dichlorophenol be deleted as a basis for listing waste K043.

The Agency disagrees with this unsubstantiated conclusion. A number of standard references, in evaluating acute toxicity, consider compounds with an oral LD<sub>50</sub> of 580 mg/kg to be "toxic". For example, "Clinical Toxicology of Commercial Products", Gleason et. al., 3rd Edition, Baltimore, Williams and Wilkins, 1969, considers compounds which have an oral LD<sub>50</sub> (as determined using by rats) in the range of 500 mg/kg to 5,000 mg/kg to be toxic to moderately toxic; however,

it should be noted that 2,4-dichlorophenol is at the higher end of the range and would tend to be considered toxic rather than moderately toxic. Additionally, in the Registry of Toxic Effects, a widely used reference book which is published by the National Institute for Occupational Safety and Health (NIOSH), guidelines for evaluating acute\* dosages differentiating relatively toxic from nontoxic substances have been set; the LD<sub>50</sub> level indicated is 5,000 mg/kg. The Agency, therefore, could continue to include 2,4-dichlorophenol as a constituent of concern in this particular listing, on the basis of acute toxicity effects alone.

Furthermore, 2,4-dichlorophenol is chronically toxic (see Background Document pp. 8-9), a point ignored by the commenter. Listing of this compound as a constituent of concern is consequently further justified.

2. The commenter pointed out that EPA's Health and Environmental Effects Profile on "Chlorinated Phenols" contains only a general discussion of chlorinated phenols, and that data on the specific dichlorophenols is lacking. While the Health and Environmental Effects Profile on "Chlorinated Phenols" does not contain a great deal of toxicity data

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\*Applies to those substances for which acute or short term toxicity characterizes the response.

on the dichlorophenols, the health and ecological effects of the dichlorophenols are discussed more fully in the specific listing background document on 2,4-D production. As there indicated, both 2,4-dichlorophenol and 2,6-dichlorophenol are toxic and 2,4-dichlorophenol is carcinogenic (based on studies in which the skin of mice is exposed to the chemical in small doses). The Agency, however, will modify the Health and Environmental Effects Profile on Chlorinated Phenols to include more of a discussion on the dichlorophenols.

3. The commenter argues that no direct mention is made of the degradability or adsorptive properties of 2,4- and 2,6-dichlorophenol in the listing background document on 2,4-D production despite the conclusion for both compounds that "the potential for degradation or elimination is high and movement is projected to be limited." (BD-13 at 209, 215 respectively.)

The Agency strongly disagrees with the commenter. In a number of places in the listing background document, the degradability/persistence, adsorptive properties and mobility of these compounds are discussed. For example, on pp. 7 and 8, several damage incidents were discussed which illustrate groundwater contamination and, thus, confirms empirically the mobility and persistence of

these compounds. A discussion on the low degradability of these compounds in soils is also included on pg. 8. Finally, in determining the solubilities of the dichlorophenols, the Agency found that their water solubilities are significant [e.g., 4,500 mg/l at 25°C and 4,600 mg/l at 20°C for 2,4-dichlorophenols] and that in groundwater (where photodecomposition is absent) these compounds would be expected to migrate and persist. With respect to the commenter's quote cited from RD-13, the Agency finds that the quote does not even relate to chlorinated phenols.

4. The commenter took objection to EPA's assertion that "very small concentrations" of 2,4,6-trichlorophenol have been lethal to freshwater fish (LC<sub>50</sub>=426 mg/l). The commenter maintains that at this level, the chemical is virtually non-toxic.

Upon scrutiny of this comment, the Agency reaffirms its position on the aquatic toxicity of 2,4,6-trichlorophenol. EPA's Draft Ambient Water Quality Criteria Document for Chlorinated Phenols (1979) reports that the LC<sub>50</sub> value for 2,4,6-trichlorophenol is 426 ug/l. This value is three orders of magnitude less than that stated by the commenter and is considered quite toxic. Relative to this, the Agency notes that an error was made in the listing background

document in reporting the LC<sub>50</sub> value of 2,4,6-trichlorophenol as 426 ng/l (pg. 10). The Agency will correct this typographical error.

Based on the forgoing discussion, the Agency will continue to list waste K043 (2,6-dichlorophenol waste from the production of 2,4-D) as hazardous and include 2,4-dichlorophenol, 2,6-dichlorophenol and 2,4,6-trichlorophenol as a basis for listing.

## **Explosives**

## LISTING BACKGROUND DOCUMENT

## EXPLOSIVE INDUSTRY

Wastewater Treatment Sludges from the Manufacture and Processing of Explosives (R)

Spent Carbon from the Treatment of Wastewater Containing Explosives (R)

Wastewater Treatment Sludges from the Manufacture, Formulation and Loading of Lead-Based Initiating Compounds (T)

Pink/Red Water from TNT Operations (R)

I. SUMMARY OF BASIS FOR LISTING

Explosives manufacturing produces wastewaters which are often sent to treatment facilities; the resulting wastewater, spent carbon, and/or wastewater treatment sludges resulting from the production of explosives have been found to contain explosive components which can pose an explosive hazard; one of the listed wastes contains the toxic heavy metal lead, and therefore, poses a toxicity hazard. The Administrator has determined that the explosives industry generates solid wastes which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. Wastewater treatment sludges from the manufacturing and processing of explosives contain significant concentrations of explosive compounds which could pose an explosion hazard.

If improperly managed, this waste could thus present a substantial hazard to human health and the environment. Therefore, this waste meets the reactivity characteristic (§261.23).

2. Spent carbon columns from the treatment of wastewater containing explosives are saturated with explosive compounds (i.e., RDX, TNT, etc.). This waste, if improperly managed, could pose a substantial health and environmental hazard due to the explosive potential of the constituents in this waste. Therefore, this waste meets the reactivity characteristic (§261.23).
3. Wastewater treatment sludges from the manufacture, formulation, and loading of lead based initiating compounds contain substantial concentrations of the toxic heavy metal lead. The lead is in a relatively soluble form, and could migrate from the disposal site into groundwater. Therefore, if this waste is improperly managed and disposed, it could pose a substantial hazard to human health and the environment.
4. Pink/red water from TNT operations contains high concentrations of the explosive compound TNT. If improperly managed, this waste could thus present an explosive hazard, resulting in a substantial hazard to human health and the environment. Therefore, this waste meets the reactivity characteristic (§261.23).

## II. OVERALL DESCRIPTION OF INDUSTRY

The explosives industry is comprised of those facilities engaged in the manufacture and load, assemble, and pack (LAP) of high explosives, blasting agents, propellants, and initiating compounds. High explosives and blasting agents are substances which undergo violent, rapid decomposition upon detonation by heat, friction, impact or shock. Initiating compounds, on the other hand, are used to initiate or detonate large quantities of less sensitive propellants or explosives.

Explosives are manufactured in both the commercial and

military sectors. Those companies (approximately 40) that commercially manufacture explosives are situated geographically in 104 facilities\* located in 30 states throughout the country.

The states with the greatest number of facilities are California, Utah, Missouri, and Pennsylvania. The military sector of the explosives industry is segregated into two groups: Government Owned and Contractor Operated (GOCO) plants and Government Owned and Government Operated plants (GOGO). The number of military plants in these two segments is estimated to be between 23 and 35. The states with major GOCO installations are Tennessee, Wisconsin, Virginia, and Illinois.

Approximate production ranges of individual explosive products are grouped below:

<u>Production</u>	<u>Production (average daily production Range while operating in lb/day)</u>
Manufacture of Explosives	1,000 to over 40,000
Manufacture of Propellants	200 to over 30,000
Manufacture of Initiating Compounds	under 1 to over 300

According to the U.S. Bureau of Mines<sup>3</sup>, total consumption of explosives and blasting agents in 1978 was approximately 1.8 million metric tons. This figure only represents domestic sales by commercial producers. Production of explosives by

\*The Bureau of Alcohol, Tobacco and Firearms lists 621 explosive manufacturers, including licensees and permittees for manufacture of explosives, distributors, users and mix and blend operators (LAP).

the military sector is not currently available.

In terms of growth, total commercial consumption of explosives and blasting agents has increased each year over the 1973-1978 period. Consumption has risen from approximately 1.3 million metric tons in 1973 to 1.8 million metric tons in 1978, representing an increase of 38 percent.

Out of the total 1978 consumption figure, consumption of "permissibles"\* and "other high explosives" were approximately 19,000 metric tons and 81,000 metric tons respectively. Over the 1973-1978 period, consumption of permissibles has fluctuated from year to year; in 1978 consumption was approximately 7 percent less than in 1973. However, consumption of permissibles is expected to increase in the future due to increased coal mining activity to satisfy energy demands. Over the same five year period, consumption of "other high explosives" has declined each year; in 1978 consumption was approximately 32 percent below 1973 levels. This downward trend is largely attributable to the increase use of water gels (permissibles in a slurry form).

A. Manufacturing Process\*\*

For the purpose of discussing specific manufacturing processes, explosives can be subcategorized into the following three groups: explosives manufacturing (for example, TNT and

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\*High explosives approved by the U.S. Bureau of Mines for the Safety and Health Administration for use in underground coal mines.

\*\*This document describes only a few processes in the explosives industry. For a more detailed description, see Reference 22.

RDX), explosives processing (for example, dynamite and nitrocellulose-base propellants) and initiating compounds (for example, lead azide).

### Explosives Manufacturing

Most explosive compounds are manufactured in a nitration reaction. The raw material varies, but always includes a nitrating acid, usually nitric acid or a mixture of nitric and sulfuric acids or nitric and acetic acids with various organic compounds (i.e., toluene, cellulose, glycerin, etc.). The major explosives produced are nitroglycerine (NG), nitroglycerine ethylene glycol dinitrate (NG/EGDN), pentaerythritol tetranitrate (PETN), nitrocellulose (NC), trinitrotoluene (TNT), cyclotrimethylene trinitramine (RDX), and cyclotetramethylene tetranitramine (HMX) (see Table 1). Figures 1 and 2 represent typical production diagrams for NG and RDX, respectively.

### Explosives Processing (Dynamite and Propellants)

Two types of explosive processes will be discussed below as examples; dynamite and nitrocellulose-base propellants.

Dynamite - Dynamite formulations are usually composed of several dry ingredients in varying proportions and nitroglycerin (see Tables 2 and 3). In the formulation of dynamite, all ingredients except for nitroglycerin and/or ethylene glycol are premixed in batch dry blenders in buildings called "dope houses". The dope and the nitroglycerine and ethylene glycol are then batch blended in the mix house. The mix is transported to packaging

houses where they are loaded into waxed cardboard boxes or plastic tubes.<sup>16</sup>

### Nitrocellulose-Based Propellants

Nitrocellulose-based propellants can be divided into single, double, and multi-based propellants. These propellants are made by colloidizing and molding processes not unlike those used in the plastics industry. Single base propellants are compositions consisting mostly of nitrocellulose with minor amounts of plasticizers, stabilizers, burning rate catalysts, etc. Double base implies nitrocellulose plus a liquid nitrate ester, usually nitroglycerin, with stabilizers, catalysts, etc.; and multi-base implies a combination of several nitrate materials such as nitrocellulose, nitroglycerin, nitroguanidine, triethyleneglycol dinitrate, with stabilizers and the like.<sup>26</sup>

### Initiating Compounds

Initiating compounds are manufactured by nitrating the starting materials (see Table 4) and precipitating the explosive. The three general steps are: (1) reacting the starting ingredients and precipitating the product in a kettle; (2) filtration; and (3) washing the product to remove impurities. Typical initiating compounds include tetracene, trinitroresorcinol (TNR), lead azide, lead styphnate, lead mononitroresorcinate (LMR), tetra and nitromannite. Figures 4 and 5 are typical flow diagrams for the production of initiating compounds, illustrating typical lead azide and lead mononitroresorcinate production schematics respectively.

B. Waste Generation and General Description

Four solid wastes generated in the explosives industry have been identified and are described below. The production and waste treatment methods which generate these wastes are not usually found in any single facility.

Wastewater Treatment Sludges from the Manufacturing and Processing of Explosives\*

Sludges are generated when wash waters pass through settling or catch basins or screens to remove particulate explosive residues. Some, but not all of the concentrated sludges are returned to the process. For clarity, explosive manufacturing and explosive processing will be discussed separately.

Explosive Manufacturing

As illustrated in Figures 1 and 2, during the manufacturing of explosive compounds, wastewaters are generated during the filtration/washing and the cleaning of the production equipment and facilities. Such wastewaters consist of particles of the explosive compound suspended in the wastewater along with solvents and cleaning agents. The particles of explosives are removed by gravity separation in catch basins or settling tanks. The resulting sludges contain significant concentrations of the explosive compound (i.e., nitroglycerine, TNT, RDX/HMX, etc.). While some of these sludges may be recycled back to the process, they are generally too

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\*Catch basin materials in RDX/HMX production was proposed as a hazardous waste on December 18, 1978 (43 FR 58959). This waste stream will not be listed in the final regulations since it is already incorporated in this listed waste stream.

contaminated with extraneous material to be reused. These sludges constitute the first listed waste stream and are marked I in Figures 1 and 2.\*

#### Explosive Processing (e.g., blasting agents and ordinance)

During the processing of explosive compounds into commercial and military explosive agents and propellants, wastewaters containing explosive compounds are produced during several operations. Among these operations are the following:

- ° Cleaning of blending, packaging and handling equipment and storage facilities;
- ° Wet milling of propellant castings;
- ° Operation of air pollution control devices which employ wet scrubbers to control emissions and dust inside production buildings;
- ° Loading, assembling and packaging of ordinance.

Treatment of these wastewaters also produces a wastewater treatment sludge.(14)

#### Spent Carbon from the Treatment of Explosives Containing Wastewaters

Because of the potential hazard that might result from the discharge of wastewater contaminated with explosives, a number of military installations employ carbon treatment

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\*The other waste which is generated (as shown in Figures 1 and 2) consists of spent acid solutions resulting from the nitration step. Acidic wastes are usually recovered for reuse following acid reconcentration or reprocessing. Presently, the Agency does not have any data to justify listing this waste. However, if these spent acids are hazardous as defined in Subpart C of Part 261, the generator would be responsible for managing these wastes under the Subtitle C regulatory control system.

of these wastewaters, which result from the loading, assembling, and packaging operations. This treatment is designed to remove organic contaminants (including those that are explosive) from the wastewater after the initial settling (see Wastewater Treatment Sludges from the Manufacturing and Processing of Explosives).

During carbon treatment, the aqueous waste is passed through chambers or columns containing activated carbon. The explosives and other organic contaminants are then absorbed into the carbon. After the carbon becomes saturated, it is removed from the chamber or column; fresh carbon is then added and the spent absorbant discarded. At this point, the carbon contains high concentrations of explosive compounds.

Wastewater Treatment Sludges from the Manufacture, Formulation and Loading of Lead-Based Initiating Compounds

During the various stages in the manufacture and formulation of lead-based initiating compounds and their fabrication into finished products, wastewater contaminated with the initiating compounds and their feedstock is produced. These wastewaters are treated in a catch basin and the resulting sludges treated with either sodium hydroxide or heat to remove any residual explosive material. However, while this process removes any possible reactivity hazard, the sludge still contains substantial quantities of leachable lead.

### Pink/Red Water from TNT Operations

During the production and formulation of TNT and TNT-containing formulations and products, an alkaline, red-colored aqueous waste is generated. This waste stream is composed of TNT purification filtrates, air pollution control scrubber effluents, washwater from cleaning of equipment and facilities, and washwater from product washdown operations (e.g., cleaning of loaded shells prior to packaging). The pink or red coloration of the waste stream results from contamination of the water with traces of TNT (solubility of TNT in water is 1 mg/liter). Red water is more concentrated, and thus more contaminated than the pink water.

### C. Quantities of Waste Generation

It is estimated that the total amount of hazardous waste generated by all commercial and GOCO facilities is approximately 21,500 tons (19,350 metric tons dry basis) per day.<sup>5</sup> Approximately eight percent of the waste is from commercial sources and 92 percent is from military and GOCO sources (Table 5).

## IV. CURRENT DISPOSAL PRACTICES

Current disposal practices for the four listed wastes may be summarized as follows:

- ° Wastewater treatment sludges from the manufacturing and processing of explosives.

In explosives manufacturing, the wastewater treatment sludges removed from the manufacturing of explosives are typically disposed of by open burning. Some plants, however, make use of percolation/evaporation ponds for

final disposal of compounds like NG, where the liquid leaches into the ground. Another technique employed by some plants is the discharge of wastewater to earthen sumps where, twice a year, the sumps are allowed to dry up and the sediments decontaminated for residual NG and DNG (dinitroglycerin); decontamination usually involves placing the explosives on the bottom of the sump and detonating the explosives.

- ° Spent carbon from the treatment of wastewater containing explosives

At present, the spent carbon are typically disposed of through open burning or incineration.

- ° Wastewater treatment sludges from the manufacture, formulation and loading of lead-based initiating compounds.

The wastewater treatment sludges are treated by boiling and/or the addition of a caustic solution, usually sodium hydroxide and aluminum, to decompose any residual explosive compounds. After treatment, the sludges are sent to a lagoon. The sludges from the lagoons are removed every few years and disposed of in a landfill.(4) In some cases, however, the sludges from the sumps and storage tanks will be sent directly to a landfill after treatment.

- ° Pink/red water from TNT operations \*

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\*The Agency is aware that under full production, AAP's have used the rotary kiln to incinerate pink and red water. However, presently the Agency does not have adequate information on the residual ash to warrant a listing.

Disposal practices that have been used include the placing of pink/red water in evaporation ponds.\*

V. DISCUSSION OF BASIS FOR LISTING

A. Hazardous Properties of the Wastes

Solid waste materials generated by the explosives industry contain a number of explosive components which, if improperly managed, could pose a substantial hazard to human health or the environment. Data presented in Tables 7-10 support the listing of these waste streams.

1. Wastewaters generated from the manufacturing and processing of explosives have been found to contain significant concentrations of explosive compounds such as nitroglycerine, nitrocellulose, TNT, RDX, HMX, and other nitrated compounds (Table 7). These explosives are highly sensitive to impact, heat, and friction. Most of these compounds are relatively insoluble in water (see Table 6); thus they are expected to settle out of the wastewater and be present in the wastewater treatment sludges. The presence of these ex-

\*The disposal of pink/red water in evaporation ponds generates a bottom sludge which is typically removed and open burned.(22) These sludges are included in the first listed waste stream (i.e., "Wastewater Treatment Sludges from the Manufacture and Processing of Explosives." The industry practice of open burning these wastes is employed because it is by far the safest method of handling these highly reactive wastes. This cautious disposal practice by the industry substantiates further the hazards posed by these wastes if they are not properly disposed of and managed.

plosives in the sludges pose a substantial explosive hazard to human health and the environment; therefore, this waste meets the reactivity characteristic (§261.23).

2. The spent carbon, when wasted, are saturated with high concentrations of explosive compounds (i.e., TNT and RDX) (Table 8). These compounds are highly reactive/explosive, and thus, the presence of these explosives in the spent carbon would thus pose a substantial hazard to both human health and the environment; therefore, this waste would meet the reactivity characteristic (261.23).

3. Wastewater treatment sludges from the manufacture, formulation, and loading of lead based initiating compounds have been shown to contain significant concentrations of lead (Table 9). This waste, if improperly managed, could pose a substantial hazard to human health and the environment. Typical industry disposal of this waste is in a landfill, which, if subjected to an acidic environment, will certainly enhance the solubility of lead and other heavy metals, since their solubility is pH dependent (i.e., solubility increases as the pH decreases).(27)

The hazard associated with the leaching of lead from improperly designed and operated landfills is the migration of this contaminant into ground and surface waters. Thus, if solids are allowed to be disposed of in areas with permeable soils, the solubilized lead could migrate from the site to an aquifer. Surface waters may also become contaminated if run-off from the landfill is not

controlled by appropriate diversion systems.

Compounding this problem, and an important consideration for the future, is the fact that should the lead escape from the disposal site, it will not degrade with the passage of time, but will provide a potential source of long-term contamination.

4. Finally, red and pink water from TNT operations have been shown to contain significant concentrations of TNT, which is an explosive (Table 10). These compounds are also highly reactive/explosive, and thus, the presence of TNT in the pink/red water would also pose a substantial hazard to both human health and the environment; therefore, this waste would meet the reactivity characteristic (§261.23).

**B. Health and Environmental Effects**

Lead is a toxic compound that could threaten the health of both humans and other organisms. The hazards associated with lead include neurological damage, renal damage and adverse reproductive effects. In addition, lead is carcinogenic to laboratory animals, and relatively toxic to freshwater organisms. It also bioaccumulates in many species. Additional information on lead can be found in Appendix A.

Hazards associated with exposure to lead has been recognized by other regulatory programs. For example, Congress designated lead as a priority pollutant under §307(a) of the Clean Water Act and an interim drinking water standard of 0.05 ppm has also been promulgated by EPA. Under §6 of the

Occupational Safety and Health Act of 1970, a final standard for occupational exposure to lead has been established.(23,24) Also, a national ambient air quality standard for lead has been announced by EPA pursuant to the Clean Air Act.(24) In addition, final or proposed regulation of the states of California, Maine, Maryland, Massachusetts, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define lead containing compounds as hazardous wastes or components thereof.(25)

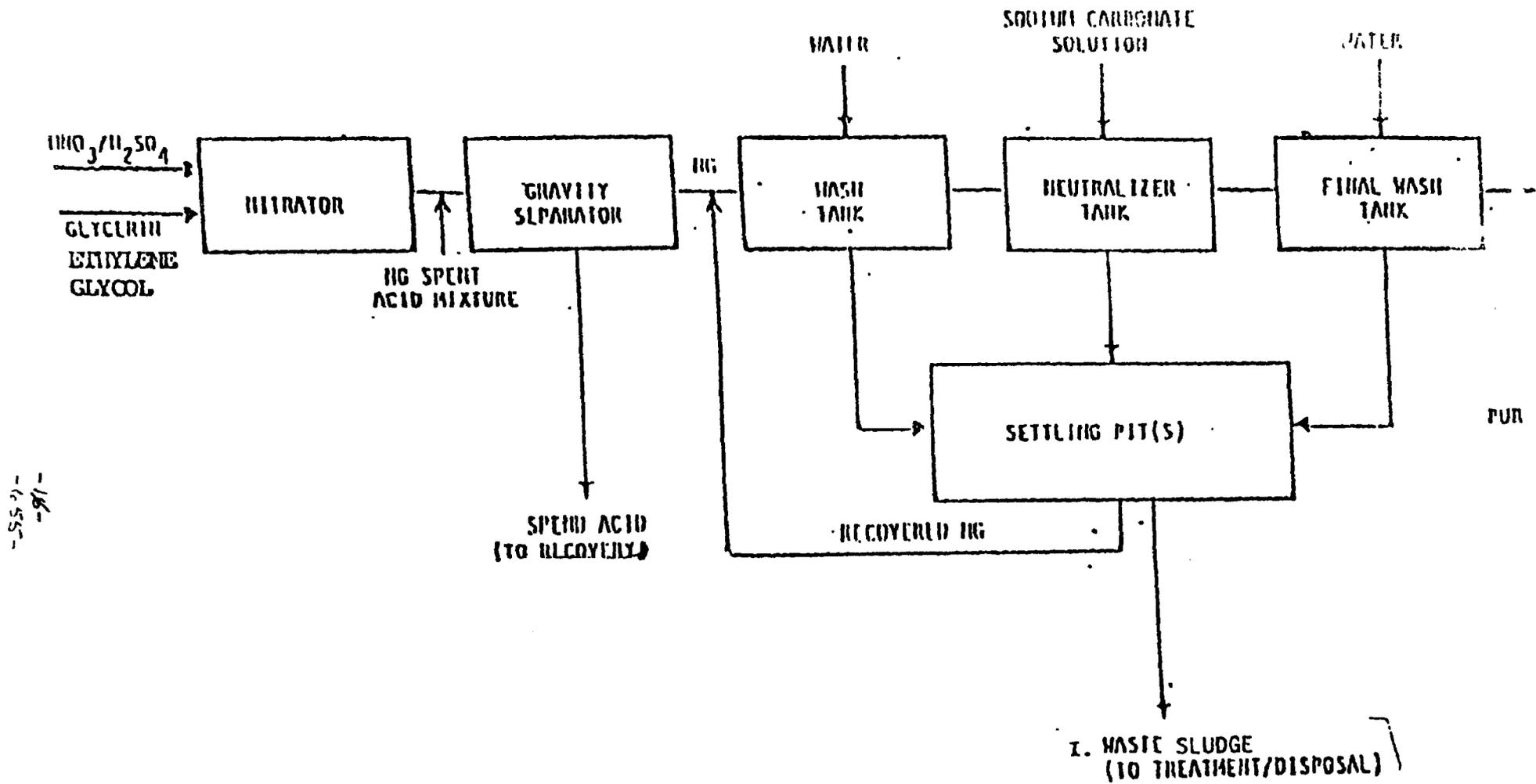


Figure 1. Schematic Flow Diagram for NG Production

Source: (5); Figure 5-31, pg. 520.

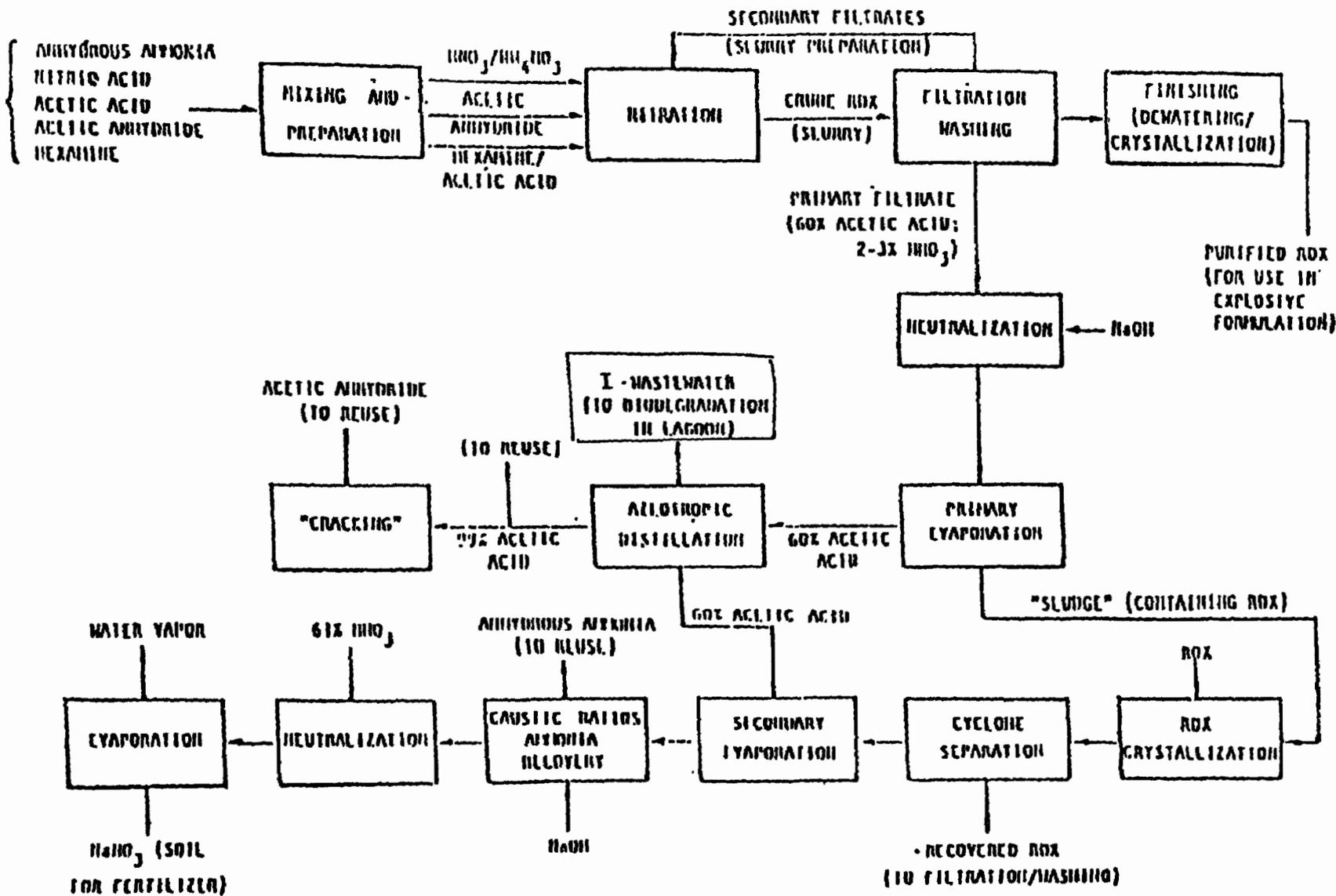


Figure 2 Schematic Flow Diagram for RDX Production.  
Source (5); Figure 5-32, pg. 5-123.

-18-  
-657-

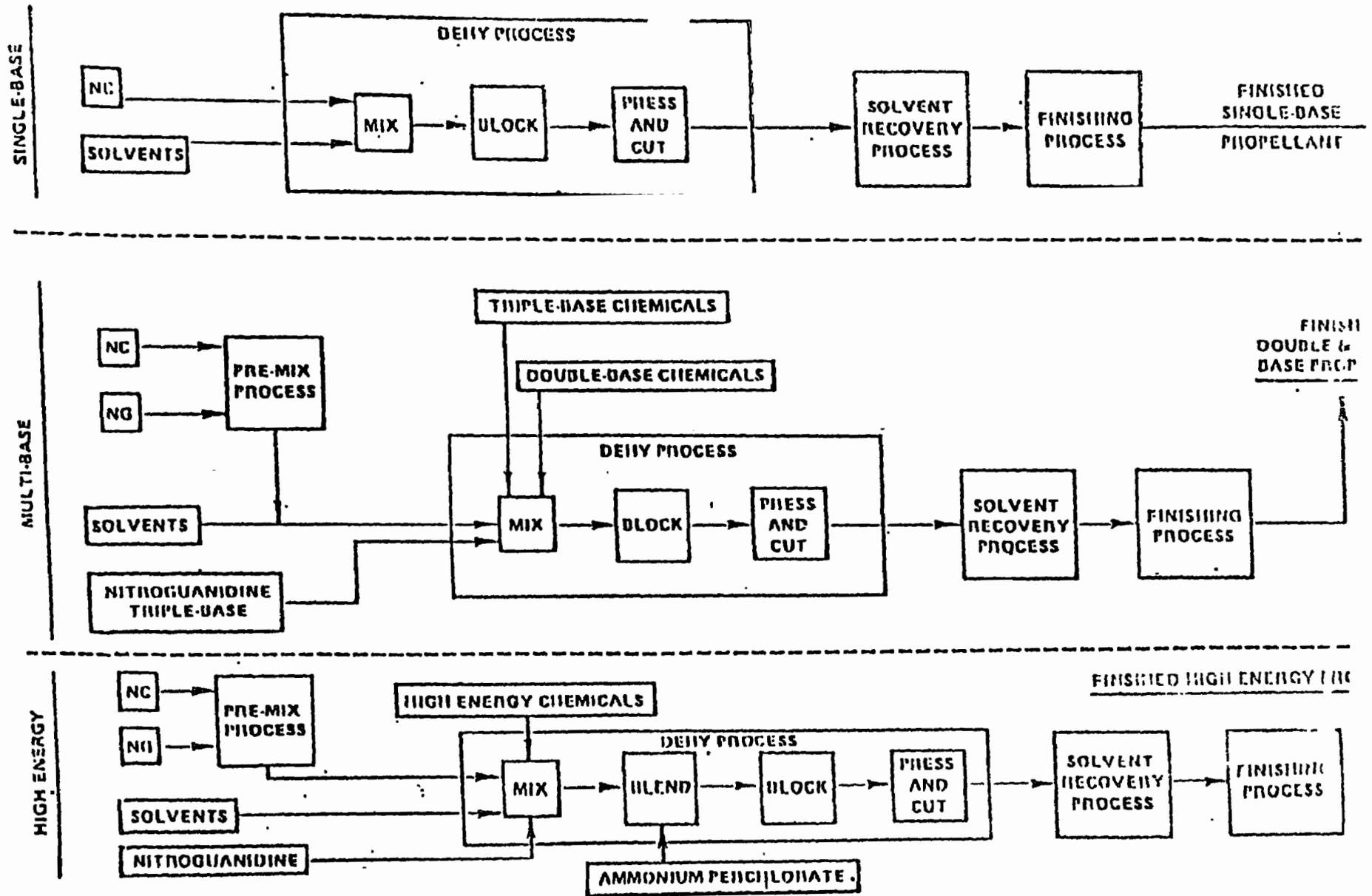


Figure 3. Solvent Propellant Production Schematic

Source: (1) Figure IV-6, pg. 50.

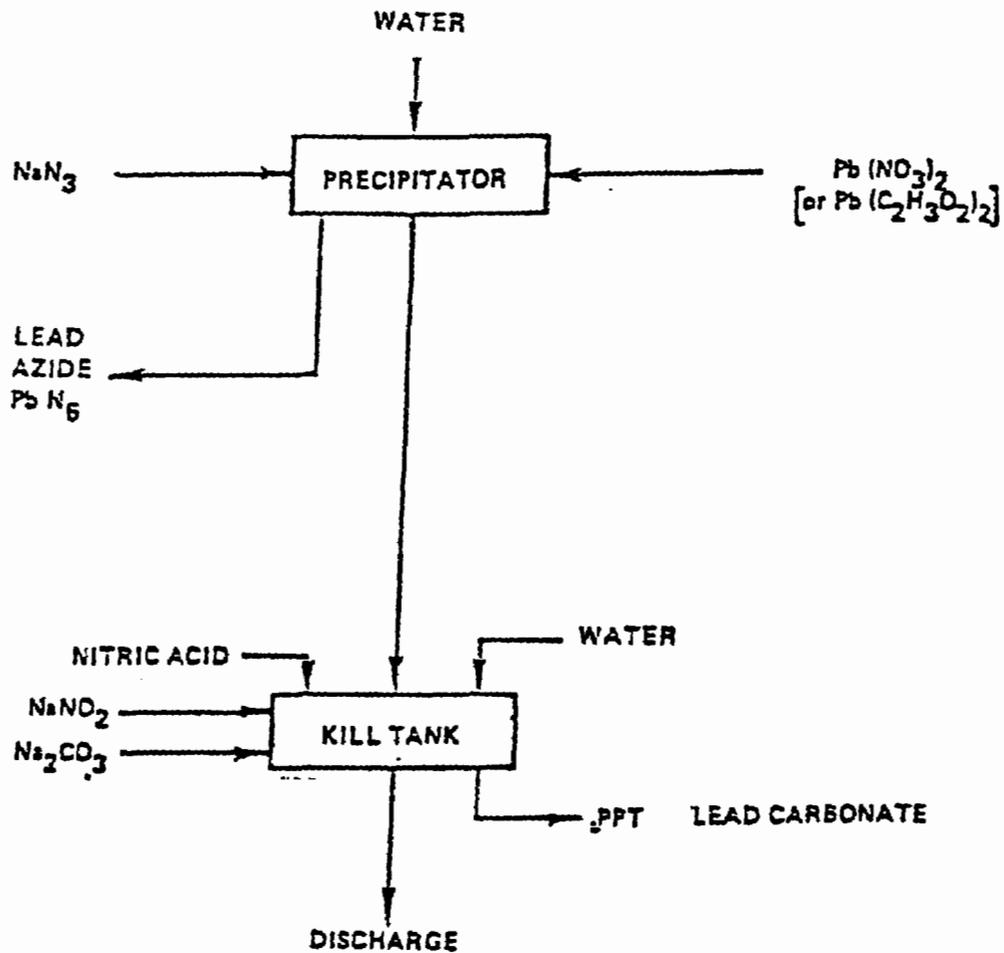


Figure 4. Typical Lead Azide Production Schematic.

Source: (2); Figure IV-8, pg. 53.

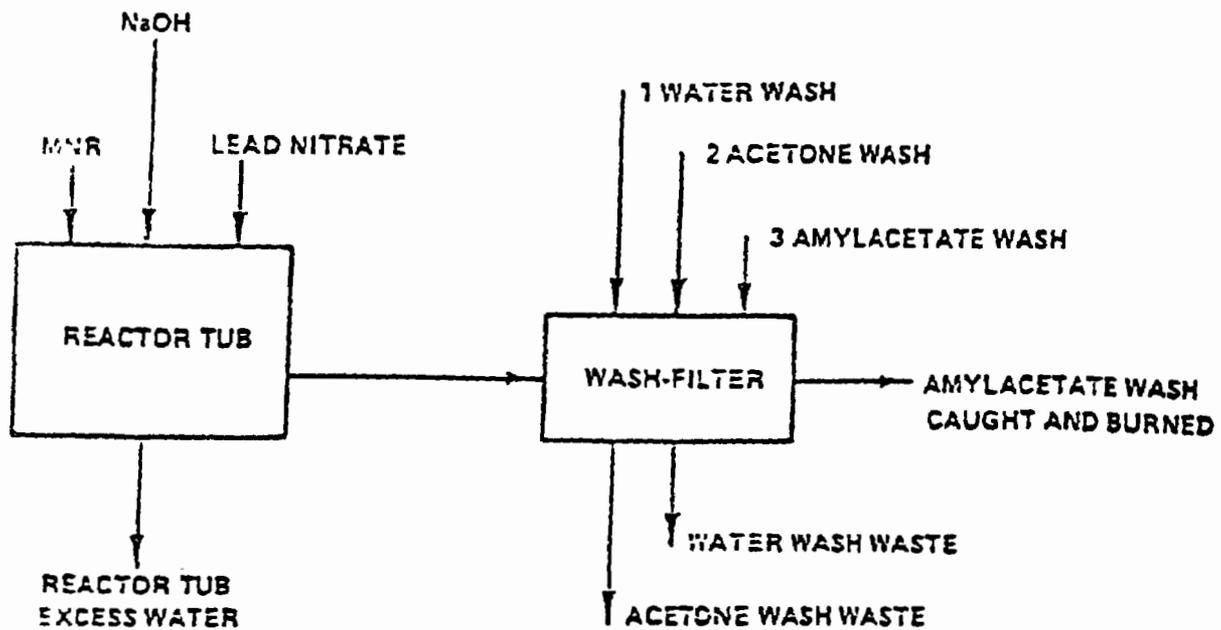


Figure 5. Typical Lead Mononitroresorcinate Production Schematic

Source: (2); Figure IV-10, pg. 57.

VII. TABLES

TABLE 1. COMMON RAW MATERIALS

<u>Compound</u>	<u>Raw Material(s)</u>	<u>Nitrating Acid</u>	<u>Additives</u>
NG	glycerine	nitric acid and sulfuric acid	ethyl acetate
NG/EGEN	glycerine ethylene glycol	nitric acid and sulfuric acid	ethyl acetate
PEEN	pentaerythritol	nitric acid	acetone
NC	cellulose	nitric acid and sulfuric acid	dibutyl phthalate phenylamine
FOX/EMX	hexamine	nitric acid and acetic acid	acetic anhydride ammonium nitrate cyclohexanone acetone
TNT	toluene	nitric acid and sulfuric acid	sodium sulfite

TABLE 2. COMMON INGREDIENTS OF DYNAMITE

Nitroglycerin  
 Barium sulfate  
 Ammonium nitrate  
 Ammonium chloride  
 Sodium nitrate  
 Sodium chloride  
 Calcium carbonate  
 Calcium stearate  
 Sulfur  
 Nitrocellulose  
 Phenolic resin or glass beads  
 Bagasse  
 Sawdust and wood flour  
 Coal  
 Corn meal and corn starch  
 Inorganic salts  
 -- Grain and seed hulls and flours

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Source: (4) page II-2.

TABLE 3. TYPICAL COMPOSITION OF DYNAMITE

<u>Component</u>	<u>Percent, wt.</u>
ammonium nitrate	50-55
nitroglycerine	15-18
sodium nitrate	0-17
<i>other</i> trace ingredients	10-35

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Source: (11) Table 7, pg.30.

TABLE 4. RAW MATERIALS FOR INITIATING COMPOUNDS

<u>Compound</u>	<u>Starting Materials</u>
Tetracene	Aminoguanidine bicarbonate, sulfuric acid, sodium nitrate
DR	Resorcinol, sulfuric acid, nitric acid
Lead azide	Sodium azide, lead nitrate or lead acetate, nitric acid, sodium nitrate
Lead styphnate	TR, magnesium oxide, lead nitrate
Nitromannite	Mannitol, sulfuric acid, nitric acid
IMR	Mononitroresorcinate, sodium hydroxide, lead nitrate
Tetryl	Nitric acid, sulfuric acid, dimethylaniline

TABLE 5: - EXPLOSIVES<sup>a</sup>

Industrial Hazardous Waste Quantities by Disposal Method						
Industry Segment	Waste Type	Total Hazardous Waste Tonnes/Year, 1977 (Dry Basis)	Disposal Methods Tonnes/Year, 1977 (Dry Basis)			
			Open Burned <sup>b</sup>	Landfilled	Sold	Other <sup>c</sup>
Private Explosives Industry:	Fixed high explosive waste	-460	>430	Negligible	<5	<26
	Blasting agents	-1,200	>1,100	Negligible	<12	<74
	Subtotals	-1,700 (-5,500-Wet Basis)	>1,500	Negligible	<17	<100
Government Owned, Contractor Operated (GOCO) Explosives Industry:	Explosive wastes	4,900	4,000	--	140	--
	Explosive contaminated inert wastes	14,700	13,700	1,000	--	--
	Other hazardous wastes <sup>d</sup>	240	90	140	20	--
	Subtotals	-19,000 <sup>e</sup>	18,600	1,140	160	--
Explosives Industry Grand Totals		-21,500 (-25,400-Wet Basis)	20,100	1,140	-100	<100

<sup>a</sup>Reference 5

<sup>b</sup>Predominantly onsite, >90 percent

<sup>c</sup>Includes chemical detoxification and subsequent disposal; usually landfill, deep well disposal, spray irrigation,

lagooning, ect.

<sup>d</sup>Includes spent activated carbon from processing aqueous hazardous wastes (open burned), red water from TNT purification (evaporated and sold), organic solvents from propellant manufacture, and wastewaters containing dissolved and suspended ROX/IMX

<sup>e</sup>Dry Basis = Wet Basis

TABLE 6  
SOLUBILITY FACTORS FOR EXPLOSIVE COMPOUNDS

<u>Compound</u>	<u>Solution</u>	<u>Solubility</u>	<u>Temperature</u>
NG	water	0.14 g/100g	25°C
	water	0.24 g/100g	60°C
SEN	water	0.68 g/100g	20°C
	acetone	very soluble	25°C
	ethyl ether	very soluble	
FEEN	water	insoluble	
FOX	water	insoluble	
Lead azide	water	0.02 g/100g	18°C
	water	0.09 g/100g	70°C
Nitronnrite	water	insoluble	
	ethanol	2.9 g/100g	13°C
	ether	4 g/100g	9°C
Lead styphnate	water	0.04 g/100g	

TABLE 7.

1. Wastewater treatment sludges from the manufacture and processing of explosives (R)

<u>Process</u>	<u>Waste (Concentration)</u>
Nitration of cellulose (Note: nitrocellulose is used in a number of industries) <sup>19</sup>	Sludge (25% water and 75% nitrocellulose) at 60 ton/yr at one plant
Nitrocellulose (NC) Production <sup>5</sup>	NC fines lost in overflow will be picked up in settle basin or other waste water sludge and is estimated at 1 metric ton (2200 lbs) per day per line or about 0.072% of NC output.
Nitroglycerin (NG) production <sup>5</sup>	NG lost to wastewater at 0.006 kg per Kg NG produced
Nitroglycerin production <sup>2</sup>	NG discharges in wastewater: as high as 1000 mg/l
TNT production <sup>2</sup>	100 mg/l of TNT to wastewater
Nitrocellulose production <sup>2</sup>	NC fines can produce levels of solids from 1000 to 10,000 mg/l
Batch Nitroglycerin Production <sup>7</sup>	Wastewater (315 to 12,700 ppm)
Combined wastewater of Radford AAP continuous NG Nitration and Spent Acid <sup>7</sup>	Nitroglycerin in wastewater (800 to 1,800 ppm)
RDX/HMX production <sup>7</sup>	Catch basins remove 33 percent of RDX and 62 percent of HMX from

TABLE 8.

3. Spent carbon from the treatment of wastewater containing explosives (R)

<u>Process</u>	<u>Waste (Concentration)</u>
LAP Melt loading of 105mm Cartridge <sup>5</sup>	Composition B* washings to Carbon Columns at a rate of 3.64 kg per 10,000 loaded rounds
LAP 40mm Cartridge <sup>5</sup>	Composition B to Carbon Columns at a rate of 0.45 kg per 10,000 loaded rounds

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\*Composition B--60% RDX. 39% TNT, 1% Wax

TABLE 9.

4. Wastewater treatment sludges from manufacture, formulation and loading of lead based initiating compounds (T)

<u>Process</u>	<u>Waste (Concentration)</u>
Initiating Compounds <sup>19</sup>	Aqueous waste containing 0.3% Pb @ at one plant that produced 300 M gal per year
Initiating compounds <sup>19</sup>	Precipitate 100%. Pb CO <sub>3</sub> , one plant produced 1 ton per year.
Initiating Compounds <sup>19</sup>	Aqueous Waste (Pb 1.2 ppm) one plant producing 12.5 M gal/yr
Production of lead azide and lead styphnate <sup>2</sup>	200 mg/l in wastewater which contributes approximately 2 lbs a day of Pb

TABLE 10.

5. Pink/red water from TNT operations (R)

<u>Process</u>	<u>Waste (Concentration)</u>
TNT Production <sup>5</sup> (batch process)	Red water solids are produced at a rate of (0.2398 kg per Kg TNT produced)
TNT Production <sup>5</sup> (continuous process)	Red water produced at a rate of 0.50 kg per kg TNT) produced which contains 6% TNT isomers and alpha- TNT
LAP <sup>2</sup>	Pink water with about 4.5% TNT (2,4,6-TNT) and by products (isomers)
TNT Production <sup>6</sup>	Red water (0.34 kg per kg produced TNT)
Evaporator Condensate <sup>7</sup> (A source of pink water)	Pink water (as high as 150 mg/l of TNT)

Note: Despite the relatively low TNT concentration of evaporator condensate, the mass discharged may be substantial. For example, at full TNT production the condensate discharged for Joliet AAP is projected at 325 gals per minute. A TNT concentration of 4 mg/l, this represents a daily-discharged of 15.6 pounds of TNT.<sup>7</sup>

## VI. References

1. Van Noordwyk, H., L. Schalit, W. Wyss, and H. Atkins. Quantification for municipal disposal methods for industrially generated hazardous wastes. EPA No. 600/2-79-135. Municipal Environmental Research Laboratory. Cincinnati, Ohio. NTIS PB No. 140 528. August, 1979.
2. U.S. EPA. Development document for interim final effluent limitations, guidelines and proposed new source performance standards. Effluent Guidelines Division, Office of Water and Hazardous Materials. Washington, D.C. EPA No. 440/176-060. March 1976.
3. Bureau of Mines, U.S. Department of the Interior. Mineral industry surveys. Explosives Annual 1978.
4. Patterson, J., N. I. Shapira, J. Brown, W. Duckert, and J. Polson. State-of-the art: Military explosives and propellants production industry. V.II. Waste characterization. EPA No. 600/2-76-213b. NTIS PB No. 260 918. August, 1976.
5. TRW Systems Group. Assessment of industrial hazardous waste practices: Organic chemicals, pesticides, and explosives industries. NTIS PB No. 251 307. April, 1975.
6. Hudak, C. E., and T. B. Parsons. Industrial process profiles for environmental use. Chapter 12, The explosives industry. NTIS PB No. 291 641. February, 1977.
7. Patterson, J., J. Brown, W. Duckert, J. Polson, and N.I. Shapira. State-of-the-art: Military explosives and propellants production industry. V.III, Wastewater treatment. EPA No. 600/2-76-213c. NTIS PB No. 265 042. October, 1976.
8. Not used in text.
9. Not used in text.
10. Not used in text.
11. Patterson, J.W., and R.A. Minear. State-of-the-art for the inorganic chemicals industry commercial explosives. EPA No. 600/2-74-009b. NTIS PB No. 265 042. March, 1975.
12. Not used in text.

13. Not used in text.
14. Hydrosience, Inc. Draft development document for proposed effluent limitations guidelines, new source performance standards and pretreatment standards for the explosives manufacturing point source category. April, 1979.
15. Not used in text.
16. U.S. EPA. The health and environmental impacts of lead and an assessment of the need for limitations. Office of Toxic Substances. EPA No. 560/2-79-001. NTIS PB No. 296 603. 1979.
17. Not used in text.
18. Not used in text.
19. State of New Jersey. Unpublished Data. Waste characterization data from the State file of "Industrial Waste Surveys". To Claire Welty of OSW. 8/31/79 and 9/4/79.
20. Not used in text.
21. Not used in text.
22. JRB Associates, Inc. Evaluation of treatment, storage and disposal techniques for ignitable, volatile and reactive wastes. U.S. EPA, OSW. Contract Number 68-01-5160 (Draft). January 17, 1980.
23. U.S. Department of Interior, Bureau of Mines. Mineral commodity summaries. 1979.
24. NIOSH. Registry of toxic effects of chemical substances. U.S. Department of Health, Education and Welfare, National Institute for Occupational Safety and Health. 1977.
25. U.S. EPA. States Regulations Files. Hazardous Waste State Programs, WH-565, U.S. EPA, 401 M St., S.W., Washington, D.C. 20460. Contact Sam Morekas. (202) 755-9145.
26. Not used in text.
27. Pourbaix, M. Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, London. 1966.
28. RCRA 3001 Docket. Memo of telephone conversation between Thomas Hess of JCAP and Chester Oszman of EPA, dated August 25, 1980.

29. RCRA 3001 Docket. Memo of telephone conversation between Major Bankowski of the U.S. Army and Chester Oszman of EPA, dated August 25, 1980.

Response to Comments - Explosives Industry

Wastewater treatment sludges from the manufacturing and processing of explosives (K044), spent carbon from the treatment of wastewater containing explosives (K045) and pink/red water from TNT operations (K047) are listed as hazardous because these wastes have been found to contain significant concentrations of explosive components which can pose an explosive hazard; thus, meets the reactivity characteristic (§261.23). One commenter disagrees with the Agency since these wastes are not reactive as determined by DOD test methods and, thus, recommends that these wastes be removed from Section 261.32.

Specifically, in reference to hazardous waste listing No. K045, the commenter stated that filtration of pink water through carbon absorption columns results in the accumulation of spent carbon (i.e., granulated carbon contaminated with TNT/RDX/HMX). Further, regular disposition of wet spent carbon is by open burning. In testing spent carbon, the results indicate that this material is insensitive to initiation when wet (25-30 percent H<sub>2</sub>O).

In reference to hazardous waste listing No. K047, the commenter has tested the waste using detonation propagation tests and reported results which have shown that aqueous slurries will not support a propagating detonation at concentrations of 30 percent or lower (i.e., less than 31% TNT in water) in either a gelled or settled condition. Similarly,

aqueous gelled slurries of RDX and HMX at concentrations of 20 percent and HMX at 5 percent or less concentration are non-propagating. Further, data on 35 percent TNT liquor indicated that the waste stream was insensitive to friction pendulum, drop weight, rifle bullet, sliding rod, and confined steel pipe tests.

Finally, for hazardous waste listing No. K044, no direct comment was put forth except that the background documentation is insufficient to support the listing and that the determination of whether it be listed should wait further documentation.

Two other points were made in the comments on the explosive listing. First, red water has been previously sold as a raw material to the paper industry and therefore is not a manufacturing by-product which has been typically discarded. Secondly, rather than a blanket inclusion of these wastes (K044, K045, and K047) in the hazardous waste list, the commenter suggests that the determination of whether and when the above listed wastes are subject to the hazardous waste rules is best made (on a case by case basis) by each generator, in light of whether his waste exhibits at any time any of the hazardous waste characteristics set forth in Subtitle C.

The Agency agrees with the commenter that those explosive industry wastewaters, wastewater sludges, and spent carbon which contain a significant amount of water will not be

readily sensitive to detonation. For example, spent carbon containing 25-30 percent or more of water and TNT sludges containing 65 percent or more of water would be difficult to detonate.

The Agency is aware, (as is the commenter) however, that a problem does arise when the spent carbon and wastewater sludges are allowed to dry; the drier the material, the more reactive the substance. This point was confirmed during a telephone discussion with the Department of Army.<sup>28,29</sup> An additional consideration is that this particular comment was restricted to TNT, HMX, and RDX, which leaves a large segment of the explosive industry without comment. For example, nitroglycerine shavings from the production of rocket motors being practically insoluble in water presents a different handling problem than the TNT liquor (red water). The milled shaving are easily separated from the water stream and may, over time, self-ignite.

Therefore, the Agency believes, in light of plausible mismanagement practices (for example, the deposition of red water in sanitary landfills or surface impoundments), that sludges, generated from the manufacturing and processing of explosives, red/pink water from TNT operations, and spent carbon from the treatment of wastewater containing explosives will dewater over time and accumulate solids thus resulting in an increased reactivity hazard. Surface impoundments

have been used in the past for the deposition of red/pink water, and a bottom sludge has accumulated over the years which tends to dry over the depth of the sludge. Further, the TNT sludge is not readily degraded, becomes reactive when dry, and is somewhat toxic. Dry TNT, is also classified as a Department of Transportation-Explosive A.<sup>24</sup>

In view of the above discussion, the Agency will maintain the current listings of the explosive industry (K044, K045, and K047). The Agency recommends that individual explosive plants who believe their waste stream(s) has properties which are fundamentally different from those which the Agency has cited in the background document as the basis for listing should file a petition for delisting in accordance with Sections 260.20 and 260.22 (petitions to amend Part 261 to exclude a waste produced at a particular facility).

LISTING BACKGROUND DOCUMENT

PETROLEUM REFINING

API Separator Sludge From the Petroleum Refining Industry (T)

Dissolved Air Flotation (DAF) Float From the Petroleum Refining Industry (T)

Primary Oil/Solids/Water Separation Sludge From The Petroleum Refining Industry (T)\*

Secondary (Emulsified) Oil/Solids/Water Separator Sludge From The Petroleum Refining Industry (T)\*

Slop Oil Emulsion Solids From The Petroleum Refining Industry (T)

Heat Exchanger Bundle Cleaning Sludge From The Petroleum Refining Industry (T)

Tank Bottoms (Leaded) From The Petroleum Refining Industry (T)

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\*Note: The Agency, on May 19, 1980, promulgated as interim final hazardous waste listings the waste streams "Dissolved air flotation (DAF) float from the petroleum refining industry" (K048) and "API separator sludge from the petroleum refining industry" (K051). The Agency is now promulgating these listings as "final-final" regulations. In addition, in response to a petition for rulemaking, the Agency is proposing to expand these listings to include additional waste streams which are said to be identical in composition because they derive from the same steps and serve the same functions in the treatment of wastewater in the petroleum refining industry. These additional listings are the other sludges from the primary and secondary treatment of wastewater in the petroleum refining industry.

Throughout this background document, the Agency now refers to all primary and secondary wastewater treatment sludges in the aggregate, thus including the API and DAF sludges. We think this approach proper, since we believe the same rationale encompasses the listing of all primary and secondary sludges. We repeat, however, that we are accepting comments on the proposed listing of the other primary and secondary wastewater treatment sludges, and we will revise this proposal to the extent it is demonstrated that other primary and secondary wastewater treatment sludges differ significantly from those generated by API separators and the DAF.

\*\*These wastes also contain concentrations of certain other heavy metals listed in Appendix VIII of Part 261. However, in the Administrator's view, the concentrations of these waste constituents are insufficient to warrant regulatory concern.

## Summary of Basis for Listing

The listed wastes discussed in this document are sludges which arise either from the treatment of wastewater generated during petroleum refining operations (i.e., primary oil/solids/water separation sludge, secondary (emulsified) oil/solids/water separator sludge and slop oil emulsion solids) or from the clean-up of equipment/storage tanks used in the refinery (i.e., heat exchanger bundle cleaning sludge and tank bottoms (leaded)). The Administrator has determined that these sludges are solid wastes which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of, or otherwise managed, and therefore should be subject to management under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. These wastes contain significant concentrations of the toxic metals, lead and chromium. In some waste streams, the concentrations of lead and chromium exceed 1,000 mg/kg (dry weight). In addition to being toxic, lead has been shown to be potentially carcinogenic and bioaccumulative; hexavalent chromium compounds are carcinogenic.
2. Large quantities (a combined total of approximately 66,610 metric tons (dry weight)) of these wastes are generated annually.
3. Chromium and lead have been shown to leach from the waste API separator sludge and DAF float in significant concentrations when subjected to a waterwashing step which simulates leaching activity. The Agency would also expect the other sludges from the primary and secondary treatment of wastewater to leach chromium and lead in significant concentrations since these sludges are likely to be identical in composition and form. Furthermore, if the last three listed wastes are disposed of in an acidic environment, the solubility of the lead will certainly be enhanced, since the solubility of this toxic metal is pH dependent (i.e., solubility

increases as the pH decreases). Most hexavalent chromium compounds are extremely water soluble at all pH values. Therefore, these metals could potentially migrate from the waste into the environment. Additionally, if these wastes are incinerated without proper air pollution control equipment, the possibility exists that lead and hexavalent chromium compounds will be released into the environment and create an air pollution problem.

4. Current disposal methods such as landfilling, land-farming, lagooning and incineration, if not properly designed and operated, can lead to the contamination of surface water and groundwater either by the overflowing of wastes or the leaching of harmful constituents from the disposal sites into the environment thereby constituting a potential substantial hazard to human health and the environment.

## Profile of the Industry

### Industry Structure

The petroleum refining industry is perhaps one of the most complex and technically sophisticated in the United States. There are some 250 to 300 refineries in the United States, ranging in size from about 400,000 BPD\* to only a few hundred BPD. These refineries vary from a fully integrated, high-complexity plant capable of producing a complete range of petroleum products and some petrochemicals, to very simple plants capable of producing only a very small number of products. Some refineries are modern and of recent construction, while others contain at least some operating process units constructed 40 or more years ago. The crude slates for refineries vary widely. The product mixes, and to some extent the product properties, also vary from refinery to refinery. Because of this, each refinery is characterized by a unique capacity, processing configuration, and product

\*BPD = Barrels per day

distribution. A survey of operating refineries in the United States between 1962 and 1972 is presented in Table 1 and the geographic distribution of these plants are shown in Figure 1.

Based on the Bureau of Mines figures for 1974, total U.S. refining capacity for 1974 was 14,486,000 BPD. As presented in Figure 2, District III\* has by far the greatest capacity (6,086,000 BPD). The four other districts, arranged in decreasing order of capacity, are District II (3,950,000 BPD), District V (2,289,000 BPD), District I (1,643,000 BPD) and District IV (518,000 BPD). (Figure 2 indicates which states are included in each region.) In the period between 1960 and 1974, Districts II, III, and V experienced the greatest growth.

A typical breakdown of refinery capacity is shown in Table 2 and indicates that a majority (55%) of the individual plants are in the size range of 10 - 100,000 BPD while a majority of total capacity (57%) lies in those facilities which are greater than 100,000 BPD.

#### Future Trends

The number of refineries in the United States has decreased in the last few decades (see Table 1), while the average size of a refinery has increased. Few new refineries have been built in the past five years; however, changes

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\* For purposes of collecting statistics on the refining industry, the U.S. have been divided into several refining regions called Petroleum Administration for Defense (PAD) districts.

TABLE 1

## SURVEY OF OPERATING REFINERIES IN THE UNITED STATES - 1962-1972

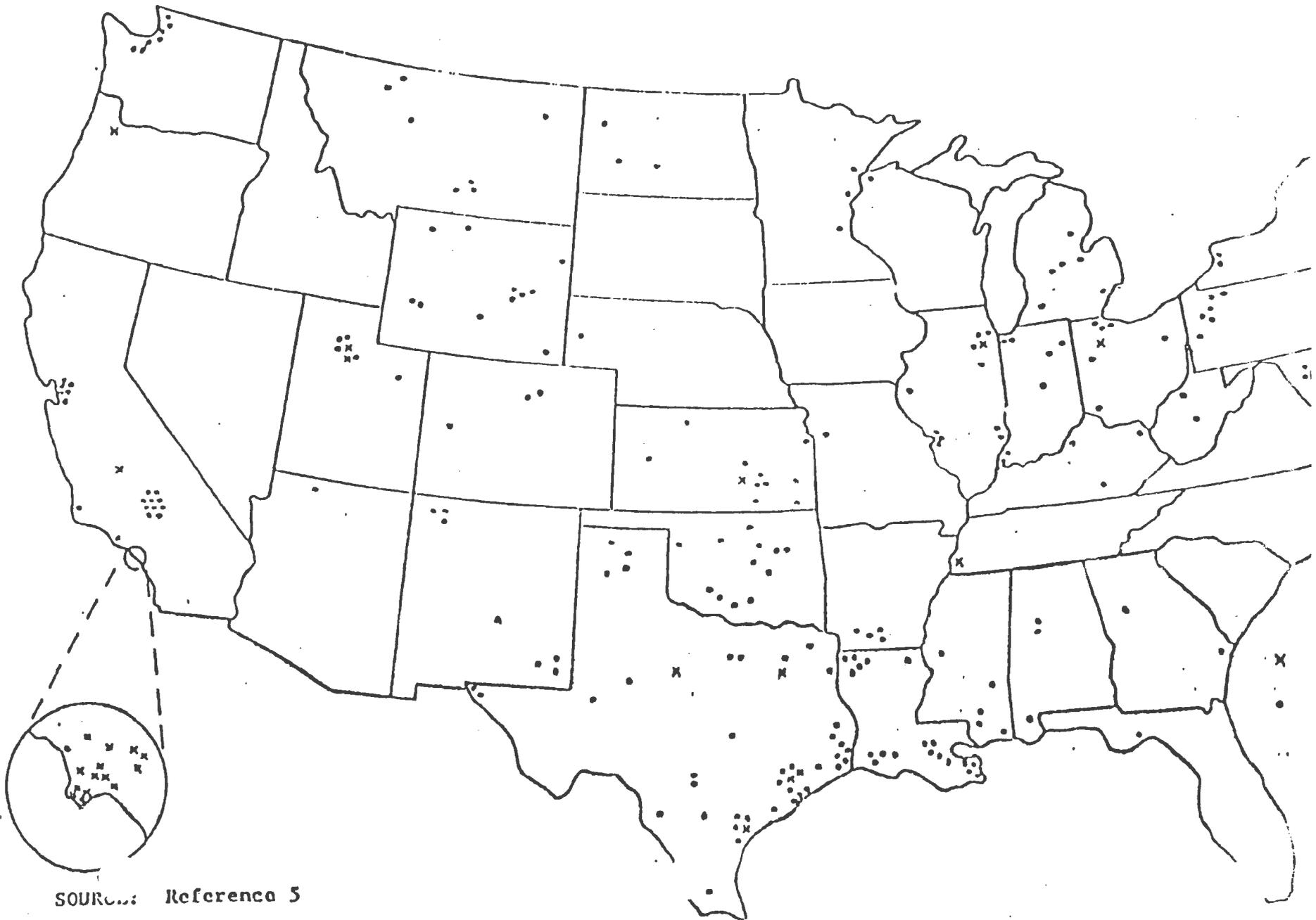
Date	Number Plants	Operating Refining Capacity <sup>1</sup>		Change Capacity (MM/SD)									Production Capacity (MM/SD)				
		(MM/CD)	(MM/SD)	Vacuum Distillation	Thermal Operation	Catalytic Cracking		Catalytic Reforming	Catalytic Hydrocracking	Catalytic Hydrorefining	Catalytic Hydrostealing	Alkylation	Catalytic Polymerization <sup>2</sup>	Tube A	Oil	C	
1/1/62	299	10.01	10.59	3.67	1.81	1.35	1.47	2.02	-	-	2.37	0.46	0.14	0.21	4.9	.	
1/1/63	293	9.92	10.46	3.58	1.75	1.89	1.55	1.99	-	-	2.54	0.49	0.13	0.20	2.9	1	
1/1/64	288	10.18	10.72	3.75	1.72	1.99	1.62	2.05	-	-	2.75	0.50	0.13	0.20	0.51	2	
1/1/65	275	10.25	10.76	3.76	1.64	1.99	1.52	2.06	-	-	2.91	0.53	0.13	0.21	0.54	2	
1/1/66	265	10.25	10.75	3.76	1.69	1.96	1.51	2.09	-	-	3.10	0.55	0.17	0.21	0.51	2	
1/1/67	261	10.45	10.95	3.89	1.64	1.95	1.55	2.12	-	-	3.25	0.60	0.13	0.21	0.54	2	
1/1/68	269	11.14	11.66	4.08	1.66	4.18	1.60	2.18	0.41	-	3.66	0.65	0.10	0.21	0.53	2	
1/1/69	263	11.57	12.08	4.12	1.60	4.25	1.55	2.54	0.50	0.55	3.27	0.67	0.25	0.20	0.57	2	
1/1/70	262	12.15	12.65	4.55	1.64	4.37	1.49	2.78	0.60	0.54	3.51	0.75	0.29	0.21	0.58	1	
1/1/71	253	12.68	13.28	4.74	1.56	4.51	1.46	2.89	0.73	0.54	3.81	0.78	0.31	0.22	0.60	.	
1/1/72	247	13.09	13.71	4.85	1.53	4.57	1.26	3.17	0.84	0.63	4.26	0.82	0.29	0.22	0.62	.	
<u>Incremental Change</u>																	
1962-1972		3.08	3.12	1.18	(0.28)	0.82	(0.21)	1.15	0.43	0.08	1.89	0.16	-	0.01	0.13	.	
2 Crude		100.0	101.3	12.8	(9.0)	26.3	(6.7)	16.9	13.8	2.6	60.6	11.5	-	0.1	4.2	.	
NRC Questionnaire																	
4. Expansion Data (MM/CD)																	
1971-1972		1.8	-	0.50	(0.19)	0.20	0.0	0.67	0.11	0.47	0.99	0.11	0.14	0.18	0.09	.	
2 Crude		100.0	-	28.0	(1.0)	11.0	0.0	12.0	4.0	12.0	35.0	2.0	8.0	1.0	5.0	.	

<sup>1</sup> MM = million barrels  
 CD = calendar day  
 SD = stream day

<sup>2</sup> Aromatic and isomerization reported beginning 1/1/69.

Source: Oil and Gas Journal, Annual Refining Reports (January 1, 1962 through January 1, 1972); NRC Refining Survey Questionnaire (1971 through 1972).

GEOGRAPHIC DISTRIBUTION OF REFINERTES



SOURCE: Reference 5

FIGURE 2

PETROLEUM ADMINISTRATION FOR DEFENSE (PAD) DISTRICTS



-683-

SOURCE: Reference 5

TABLE 2

SURVEY OF U.S. REFINING INDUSTRY  
BY CAPACITY AND NUMBER OF PLANTS

<u>PLANT SIZE, BPD:</u>	<u>Under</u> <u>10,000</u>	<u>10,000-100,000</u>	<u>Over</u> <u>100,000</u>
No. of plants	74	141	44
Total Refining Capacity, 1,000 BPD	348	6,032	8,465
% of Plants	28	55	17
% of Capacity	2.3	40.7	57.0

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Source: The Oil and Gas Journal, Annual Refining Survey (1975).

have been made in existing refineries to reflect changing technology and product demand, largely through expansion and revamping of units of existing refineries. Although there are several new facilities in the planning stages, many such projects have been either cancelled or greatly delayed primarily because of the uncertainty caused by unresolved energy and environmental issues.

Growth in petroleum demand within the next 10 years is expected to be lower than historical growth rates, thus reducing projected waste generation rates for the industry.\*

#### Processing Operations

A petroleum refinery is a complex combination of interdependent operations engaged in the separation of crude oil by molecular cracking, molecular rebuilding and solvent refining, to produce a varied list of intermediate and finished products, including light hydrocarbons, gasoline, diesel and jet fuels, light distillate fuel as well as heavy residual fuel oil. During the processing of the crude oil, a number of waste streams are generated either from the clean-up of equipment/storage tanks used in the refining process or from the treatment of wastewater generated during petroleum refining operations. The remainder of this document will discuss these particular waste streams and provide reasons

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\*Projected decrease in growth is due to a number of factors: (1) improved fuel economy for automotive engines (2) the trend among consumers to purchase smaller cars (3) slow down in jet fuel (4) rapid increase in the construction costs of petroleum refineries and (5) scarcity of capital (Reference 5).

for identifying these wastes as hazardous. (A detailed description of the petroleum refining process is not included in this document. However, to assist the reader in understanding some of the basic processing operations carried out in a petroleum refinery, a brief description of some of the individual operations is included as Attachment I.)

### Waste Generation and Management(1)

#### 1. Waste Streams

The five waste streams listed as hazardous are:

- o Primary oil/solids/water separation sludge
- o Secondary (emulsified) oil/solids/water separator sludge
- o Slop Oil Emulsion Solids
- o Heat Exchanger Bundle Cleaning Sludge
- o Tank Bottoms (Leaded)

Lead and hexavalent chromium are the constituents of concern in these waste streams. Lead in the waste streams comes predominantly from the use of tetraethyl lead in the blending of leaded products. Chromium in the waste stream comes predominantly from blowdown of cooling towers that use hexavalent chromium compounds as a corrosion inhibitor.\* Concentration ranges for lead and total chromium in representative samples of each waste are presented in Table 3.

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\*The Agency recognizes that refineries not implementing these systems will have lower concentrations levels of these toxic metals. The delisting provisions of §260.20 and 260.22 are available to generators with fundamentally different waste streams to justify delisting of their wastes.

Primary oil/solids/water separation sludge - The primary oil/solids/water separator provides for primary refinery wastewater treatment. The separators are usually connected to the oily water plant sewer. As a result, the resultant sludges contain a mixture of all sewered waste, including tank bottoms, boiler blow-down, desalter wastes, and also traces of all chemical elements which enter the refinery process.

Oil that is present in the sludge will most likely be present in the form of heavy tars since the surface oil is skimmed periodically from the primary oil/solids/water separator. Oil content of the sludge is approximately 23% by weight while water and solids constitute approximately 53% and 24%, respectively. Most of the solids content is silt and sand, but a significant amount of heavy metals are also present in the sludge.

This waste stream is listed because it contains significant concentrations of the two metals, chromium (presumably in part hexavalent, since it derives from cooling tower blowdown) and lead. (Table 3 lists the concentration ranges of the constituents of concern in each waste stream.)

Secondary (emulsified) oil/solids/water separator sludge -

Some refineries utilize secondary treatment of their wastewater (i.e., dissolved air flotation (DAF), induced air flotation (IAF), parallel plate flotation separators, etc.) following separation in the primary oil/solids/water separator to

TABLE 3

RANGE\* IN CONCENTRATION\*\* FOR CONSTITUENTS OF CONCERN

-----  
 <-----SOURCE----->  
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<u>Contaminant</u>	<u>API*** separator</u>	<u>DAF****</u>	<u>Slop Oil</u>	<u>Bundle Sludge</u>	<u>Tank Bottoms</u>
No. of Samples	12	5	9	2	2
Chromium	.10-6,790	28-260	1-1,750	310-311	-
Lead	.25-1,290	2.3-1,250	.25-580	-	158-1,420

\*Range values represent high and low concentrations for samples of each waste stream

\*\*Concentration in mg/kg dry weight, including inert solids but excluding oil

\*\*\*API separator is only one of many processes which function as a primary oil/solids/water separator

\*\*\*\*DAF is only one of many processes which function as a secondary (emulsified) oil/solids/water separator

SOURCE: Reference 1

remove additional oil and solids. The process brings finely divided oil and solid particles to the surface where they are skimmed for disposal.

Water typically constitutes 82% by weight of this waste stream, while oil and solids constitute approximately 12.5% and 5.5% respectively. The solids are generally fine silts which did not have sufficient residence time in primary separators to settle; the waste stream contains the toxic metals chromium (presumably in part hexavalent, again derived mostly from cooling tower blowdown) and lead, for which it is listed.

Slop Oil Emulsion Solids - The skimmings from the primary oil/solids/water separator generally consist of a three-phase mixture of oil, water and a third emulsified layer. The oil is returned to crude storage, the water discharged to the wastewater treatment system, while the emulsion (oil, water and solids) becomes a process waste stream. A typical combination of the waste stream by weight is 40% water, 43% oil and 12% solids. Among the solids are compounds of the metals chromium (presumably in part hexavalent) and lead, for which the waste is listed.

Heat Exchanger Bundle Cleaning Sludge - Heat exchanger bundles are cleaned during plant shutdown to remove deposits of scale and sludge. Depending upon the characteristics of the deposits, the outside of the tube bundles may be washed,

brushed, or sandblasted, while the tube interiors can be wiped, brushed, or rodded out. Sludge resulting from the cleaning process has approximately 53% water, 11% oil and 36% solids.

These solids are composed largely of silt precipitated from the water. The metals present are mostly corrosion products or scale deposits from the heat exchanger bundle tubes. Chromium presumably partly in hexavalent form, is present in the waste in substantial concentrations, and the waste is listed due to the presence of this constituent.

Tank Bottoms (Leaded) - The petroleum products (or fractions) after being separated in the distillation column have to be cooled before they are sent out or used for making other by-products. This is done in product storage tanks. As cooling occurs, the water separates from the hydrocarbon phase and is continually drained from the tanks to the refinery water treatment system. Solids formed as products of corrosion and rust in the tanks contain toxic metals, and are periodically removed. This waste is being listed because it contains lead.

In summary, the contaminants in these wastes which caused EPA to identify these wastes as hazardous are as follows:

Primary oil/solids/water separator sludge - hexavalent chromium and lead

Secondary (emulsified) oil/solids/water separator sludge - hexavalent chromium and lead

Slop Oil Emulsion Solids - hexavalent chromium and lead

Heat Exchanger Bundle Cleaning Sludge - hexavalent chromium

Tank Bottoms (leaded) - lead

## 2. Waste Generation Ratio and Composition

Many factors can affect the quantity and quality of individual waste streams. Factors that affect quality include crude oil characteristics, composition of process wastewater, occurrence of spills and leaks, composition of cooling water blowdown, use of corrosion inhibitors and the use of tetraethyl lead for specific products and modifications. In particular, it is expected that the concentration of sulfite in these wastes (and therefore the proportion of hexavalent chromium in their chromium loadings) will vary with the feedstocks used. Factors that affect both the quantity and quality of the individual waste stream include the refinery size and age, the segregation of refinery oil drains, and the actual quantity of process wastewater (Reference 2).

The constituents of concern in the individual waste streams are shown in Table 3. As this data illustrates, although each waste stream varies with regard to lead and chromium concentrations, these metals are found generally in high concentrations with some levels exceeding 1000 mg/kg dry weight.\* The reference for the data in Table 3 reports analyses for total chromium, but infers the presence of more of this element in the trivalent form. This reference was based on knowledge of the process, possible reductive reactions (e.g. by algae, as a consequence of corrosion inhibition, or the

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\*The Agency is aware that these wastes generally contain very high concentrations of zinc. Zinc is one of the secondary drinking water standard parameters, with an MCL of 5 mg/l. At this time, however, the Agency does not believe that exposure to concentrations of zinc which may leach from the waste will result in a human health hazard, and therefore is not presently designating zinc as a constituent of concern in these wastes.

presence of chromates). (12) Since the chromium in these wastes derives solely from (hexavalent) chromates, and the assumed reductive reactions are only incidental, we strongly believe that significant concentrations of hexavalent chromium will be present in the waste.

The estimated quantities of individual waste streams range from 600 - 33,000 kkg per year (dry weight) (including inert solids but excluding oil). The combined total estimated quantity is 66,610 kkg per year (dry weight) (including inert solids but excluding oil) based upon capacity of 14,200,000 BPCD\*.

The relative quantities of waste for the individual waste components for each waste stream, shown in Table 4, indicate that the primary oil/solids/water separator, slop oil and the secondary (emulsified) oil/solids/water separator are the major waste generating streams in terms of quantity. Additionally, the data indicates that chromium (presumably largely in the hexavalent form) and lead are present in substantial quantities in these wastes.

A second source of data, the American Petroleum Institute (API), performed an extensive survey of the quantities of each waste component present in two of the waste streams from Petroleum Refining Processes.

\*BPCD - Barrels per Calendar Day

As shown in Table 5, the API data on the API separator sludge\* and the dissolved air flotation (DAF) float\* generally supports the data found in Table 3. (It is important to recognize that the API data reflects a much larger sampling effort relative to that encompassed in the EPA survey.)

Current Disposal Practice - There are currently four principal methods for disposing of petroleum refinery solid wastes. These processes include land treatment, landfilling, lagooning and incineration, and may be conducted either on-site or off-site, depending upon the particulars of a given operation.

The results from both the EPA and API studies are presented in Table 6 to provide comparisons regarding the disposal methods currently employed for refinery wastes. Land treatment and landfilling appear to be the most widely employed disposal processes.

#### Hazards Posed by Waste

As indicated earlier (Table 3), the five waste streams for the petroleum refining industry contain significant concentrations of the toxic metals lead and chromium, (presumably partly in hexavalent form), with some levels exceeding 1,000 mg/kg (dry weight). Additionally, information submitted by the API for two of the waste streams (API separator sludge and the DAF float) in which a water-washing step was conducted to simulate leaching (see Table 7), indicates that lead and

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\*As already indicated, API separators and DAF are only one of many processes which derive from the same step and serve the same function in the treatment of wastewater as other primary oil/solids/water separators and secondary (emulsified) oil/solid/water separators, respectively.

TABLE 4

TOTAL QUANTITIES OF EACH WASTE COMPONENT

Metric Tons/Yr (Dry Weight)\*,\*\*

	Primary oil/solids water separation sludge	Secondary (emulsified) oil/solids/ water separator sludge	SLOP OIL	HEAT EXCHANGER SOLIDS	TANK BOTTOMS	TOTAL
chromium	17.6	8.4	17.7	.4	--	44.2
lead	1.2	.5	.06	--	1.1	2.9

SOURCE: Reference 1

Excludes inert solids and oil

Even though the quantity of heavy metals from any one waste generated at any particular petroleum refinery may be small, these wastes are normally disposed of together; therefore, the total contribution and impact of these heavy metals at any individual refinery would be substantial.

TABLE 5

RESULTS OF API SURVEY

	TOTAL WEIGHT METRIC TONS/YR		CONCENTRATION mg/kg	
	API separator sludge***	DAF****	API*,*** separator sludge	DAF**,****
Chromium	8.6	5.3	0-10,800	0-3000
Lead	2.4	.23	0-6200	0-540

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\*Sample size ranges from 63-68

\*\*Sample size ranges from 13-15

\*\*\*API separator is only one of many processes which function as a primary oil/solids/water separator

\*\*\*\*DAF is only one of many processes which function as a secondary (emulsified) oil/solids water separator

SOURCE: Reference 3

TABLE 6  
DISPOSAL METHODS FOR REFINERY WASTES<sup>a</sup>

<u>Disposal Method</u>	<u>EPA Survey<sup>b</sup></u>		<u>API Survey<sup>c</sup></u>	
	<u>On-Site</u>	<u>Off-Site</u>	<u>On-Site</u>	<u>Off-Site</u>
Landfill	5	14	47	36
Lagoon	3	2	15	4
Incineration	1	0	3	0
Land Treatment <sup>d</sup>	10	0	27	3

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<sup>a</sup>Reported in terms of number of refineries.

<sup>b</sup>Nineteen refineries reported.

<sup>c</sup>Seventy-five refineries reported.

<sup>d</sup>Percent refineries using land treatment on-site plus off-site, Jacobs 10 of 19 equal 53 percent, API 30 of 75 equals 40 percent.

SOURCE: Reference 3.

TABLE 7

MEAN WASTE EXTRACT CONCENTRATIONS (WATER EXTRACTNANT)  
(mg/l)

<u>Contaminant</u>	<u>API<sup>*,***</sup></u>	<u>DAF<sup>** ,****</sup></u>
Chromium (total)	1.9	3.3
Lead	2.3	2.1

\*Sample size: 60-63

\*\*Sample size: 12-15

\*\*\*API separator is only one of many processes which function as a primary oil/solids/water separator

\*\*\*\*DAF is only one of many processes which function as a secondary (emsulfied) oil/solids/water separator

SOURCE: Reference 3.

chromium will leach from the waste in significant concentrations (between 10 and 100 times the National Interim Primary Drinking Water Standard) even when these metals are subjected to mild environmental conditions. In view of the relative insolubility of trivalent chromium compounds (see Attachment II), the water-extractable chromium in these wastes points to the presence of hexavalent chromium. In many cases, off-site waste disposal is implemented and these sites may be characterized by acidic environments (for instance, if they contain domestic refuse or other acidic wastes) in which case the hazardous constituents would be released for environmental migration.

Although leaching data for the other waste streams (including other sludges from the primary and secondary treatment of wastewater) is not presently available, the Agency believes that the contaminants found in these wastes would also tend to migrate from the waste based on the solubility of the contaminants. An additional factor supporting this belief is the fact that chromium and lead have been shown to migrate in significant concentrations from the API separator sludge and DAF float, and since the other waste streams are of roughly similar composition and are generated as part of the same production process, migration patterns of these similar waste streams can be readily anticipated. Solubilization of lead is pH dependent, and increases as the pH of the solubilizing medium decreases.<sup>(8)</sup> If the sludges are exposed to acidic conditions (which could occur due to co-disposal with waste

acids, or in municipal landfills or in areas where acid rain is prevalent) this toxic metal could be released from the waste matrix. Furthermore, lead hydroxide, present in these wastes<sup>(2)</sup>, is sufficiently soluble to exceed the National Interim Primary Drinking Water Standard (NIPDWS) of 0.05 mg/l<sup>(11)</sup>. Hexavalent chromium compounds are highly soluble and mobile (Attachment II).

Once released from the matrix of the waste, lead and chromium can migrate from the disposal site to ground and surface waters utilized as drinking water sources. Present practices associated with landfilling, land treatment or impounding the waste may be inadequate to prevent such an occurrence. While the Agency is presently unaware of all management practices employed for these wastes, since there are a great number of generating and management sites and because wastes that are disposed of off-site out of the generator's personal supervision are particularly susceptible to mismanagement, there is a strong likelihood that some of these wastes are not properly managed in actual practice. One example of inadequate management would be improper selection of disposal sites in areas with permeable soils, permitting contaminant-bearing leachate from the waste to migrate to groundwater. This is especially significant with respect to lagoon-disposed wastes because a large quantity of liquid is available to percolate through the solids and soil beneath the fill.

An overflow problem might also be encountered if the liquid portion of the waste has been allowed to reach too high a level in a lagoon. Under these circumstances, a heavy rainfall could cause flooding which might reach surface waters in the vicinity.

In addition to difficulties caused by improper site selection, unsecure landfills are likely to have insufficient leachate control practices. There may be no leachate collection and treatment system to diminish leachate percolation through the wastes and soil underneath the site to groundwater, and there may be no surface run-off diversion system to prevent contaminants from being carried from the disposal site to nearby ground and surface waters, thereby increasing the likelihood of drinking water contamination. Further, once lead and chromium have escaped from the disposal site, they will persist in the environment (in some form) for virtually indefinite periods, since they are elements and not subject to degradation.

Additionally, if these wastes are incinerated without proper air pollution control equipment, the possibility exists that lead (a volatile heavy metal\*) will be released into the environment and create an air pollution problem. Also, incineration of chromium-bearing wastes results in the oxidation of chromium to the carcinogenic hexavalent form.

A further possibility of substantial hazard arises during

transportation of these wastes to off-site disposal facilities. This increases the likelihood of their being mismanaged, and may result either in their not being properly handled during transport or in their not reaching their destination at all, thus making them available to do harm elsewhere. A transport manifest system combined with designated standards for the management of these wastes will thus greatly reduce their availability to do harm to human beings and the environment.

The Agency has determined to list these wastes as hazardous wastes on the basis of lead and hexavalent chromium constituents, even though these constituents are also measurable by the characteristic of extraction procedure toxicity.\*\* Although the concentrations of these constituents in an EPA extract of wastes from individual sites might be less than 100 times the National Interim Primary Drinking Water Standards, the Agency, nevertheless, believes that there are factors in addition to metal concentrations in leachate which justify the T listing. Some of these factors already have been identified, namely the significant concentrations of chromium (presumably in part in hexavalent form) and of lead in the

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\*An incinerator operating to destroy organic materials operates in the range of 1000° C - 1200° C. This would cause lead to evaporate out of the equipment as fast as water would evaporate at 11° C. The temperature at which vapor pressure equals 10 mm Hg for water is 11° C and for lead is 1162° C (11).

\*\*Hexavalent chromium, although not currently measurable by the characteristic of EP toxicity, the Agency has proposed to amend to characteristic of EP toxicity to apply to hexavalent chromium rather than total chromium (45 FR 72029, October 30, 1980).

five waste streams, the non-degradability of these substances, and the possibility of improper management of the wastes in actual practice.

The quantity of these wastes generated (a combined total of approximately 66,610 metric tons dry weight) is an additional supporting factor. As previously indicated, the wastes from petroleum refining industry contain significant concentrations and quantities of chromium and lead. Large amounts of these metals from the five waste streams are thus available for potential environmental release. The large quantities of these contaminants pose the danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time, since large amounts of pollutants are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or used up due to the large quantities of pollutant available. All of these considerations increase the possibility of exposure to the harmful constituents in the wastes, and in the Agency's view, support a T listing.

#### Health Effects of Waste Constituents of Concern

Toxic properties of chromium and lead have been well documented. Hexavalent chromium is toxic to man and lower forms of aquatic life. Lead is also poisonous in all forms. It is one of the most hazardous of the toxic metals because it accumulates in many organisms, and its deleterious effects

are numerous and severe. Lead may enter the human system through inhalation, ingestion or skin contact. Improper management of these sludges may lead to ingestion of contaminated drinking water. Additional information on adverse health effects of chromium and lead can be found in Appendix A.

The hazards associated with exposure to lead and chromium have been recognized by other regulatory programs. Lead and chromium are listed as priority pollutants in accordance with §307 of the Clean Water Act of 1977. Under Section 6 of the Occupational Safety and Health Act of 1970, final standards for Occupational Exposure have been established and promulgated in 29 CFR 1910.1000 for lead and chromium. Also, a national ambient air quality standard for lead has been announced by EPA pursuant to the Clean Air Act (9). In addition, final or proposed regulations of the States of California, Maine, Massachusetts, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define chromium and lead containing compounds as hazardous wastes or components thereof (10).

## References

1. Jacobs Engineering Company. Assessment of hazardous waste practices in the petroleum refining industry. NTIS PB. No. 259 097. June, 1976.
2. Jacobs Engineering Company. Alternatives for hazardous waste management in the petroleum refining industry. OSW Contract Number 68-01-4167. Unpublished data. July, 1977.
3. Engineering-Science Inc. The 1976 API refinery solid waste survey, prepared for the American Petroleum Institute. April, 1978 - 4 parts.
4. Radian Corporation. Environmental problem definition for petroleum refineries, synthetic natural gas plants and liquified natural gas plants. EPA No. 68-02-1319. NTIS PB No. 252 245. November, 1975.
5. A.D. Little, Inc. Environmental considerations of selected energy conserving manufacturing process options. Vol. IV. Petroleum refining industry. EPA No. 600/7-76/034-d. NTIS PB No. 264 270. December, 1976.
6. U.S. EPA. Effluent Guidelines Division. Development document for effluent limitations guidelines and standards for the petroleum industry. EPA No. 440/1-79/014-b. December, 1979.
7. The Merck Index, 8th ed. Merck & Co., Inc. 1968.
8. Pourbaix, M. Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, London. 1966.
9. U.S. Department of Interior, Bureau of Mines. Mineral commodity summaries. 1979.
10. U.S. EPA State Regulations Files. Hazardous Waste State Programs, WH-565, U.S. EPA, 401 M St., S.W., Washington, D.C. 20460. Contact Sam Morekas (202) 755-9145.
11. CRC Handbook of Chemistry and Physics, 56th ed. CRC Press, Cleveland, Ohio. 1975.
12. Memorandum from J. Bellin (OSW), to Docket, dated October 8, 1980.

Wastes from Petroleum Refining Process - Response  
to Comments from Proposed Regulations

(December 18, 1980)

i. A number of commenters stated that the proposed listing "SIC 2911 API separator sludge (T,O)" should not apply to all wastes from API separators but only to waste generated from petroleum refineries\*. The commenters argued that API separators are used in numerous industries and processes (i.e., the food industry, soap and detergent industry, etc.) which generate sludges of widely differing characteristics. These separators, however, do not necessarily generate a hazardous waste (i.e., the term does not automatically suggest that the sludge from any use of such a piece of equipment would be a hazardous waste). Therefore, the commenters want the listing to be either clarified to indicate that the API separator sludge is meant to be specific to separators used in the petroleum refining industry; or otherwise, want the process deleted from the hazardous waste list in Section 250.14.

- o The Agency agrees with the commenters. The listing has therefore been clarified to indicate that the API separator sludge is meant to be specific to separators used in the petroleum refining industry.

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\*A note appeared before the listed waste in §250.14 which specified that the SIC code used in the listing was for ease of reference only. Thus, the SIC classification of the industry generating the waste would have no effect on the listing of that process waste as hazardous.

2. One commenter suggested that additional wastes from the petroleum refining industry be added to the hazardous waste list. These wastes included: (1) petroleum refining sulfur removal, (2) petroleum refining wastewater treatment sludges, (3) petroleum refining boiler cleaning, (4) petroleum refining alkylation\* and (5) petroleum refining-coke from asphalt cracking. Data was submitted along with the suggested listings.

- o After evaluating all the available data on the additional listed wastes, the Agency has decided not to add these wastes at the present time due to the lack of supporting data. However, the Agency will reconsider these listings at some later time once sufficient data becomes available.

3. One commenter objected to the proposed listing "SIC 2911 Petroleum refining lube oil filtration clays" due to the lack of supporting data.

- o The Agency, in re-evaluating the available data, has decided to defer the listing "SIC 2911 Petroleum refining lube oil filtration clays" until additional data is collected by the Agency on which to make a decision.

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\*This waste was listed in the December proposal (43 FR 58959).

## Attachment I

The refinery process can be categorized into the following individual operations which are displayed schematically in Figure A-1.

- o Separation
- o Treating
- o Conversion
  - o cracking
  - o combination
  - o rearrangement
- o Blending
- o Auxiliary Process
- o Storage

### Separation

The individual process steps and operation in this area include:

- o Topping Unit - This unit separates the crude in an atmospheric stage. The process streams from this unit normally include fuel gas, naphtha, middle distillates, and distilled fuel oil. The naphtha may be split into light and heavy fractions and the fuel oil into light, middle, and heavy distillate components.

- o Vacuum Towers - Vacuum towers are utilized for separation of the heavier fractions from the entire crude stream. For a comparable crude input, these units are capable



of producing a broader spectrum of process streams than a topping unit. For example, these units may either recover additional gas oil from the reduced crude while producing a heavy vacuum residual or may separate the reduced crude into special lube oil cuts with an accompanying residual stream. One of two stages may be utilized, depending upon the individual end-product requirement.

- o Light Ends Recovery - This operation is sometimes referred to as vapor recovery and involves the separation of refinery gases from the crude distillation unit and other units into individual component streams. The separation phase is accomplished by absorption and/or distillation, depending upon the desired purity of the product stream.

#### Treating

- o Gas Treating - The major component of the various species separated in the crude distillation unit or produced in the various processing units is hydrogen sulfide. Acid gases, such as  $H_2S$ , normally are removed from the light ends fraction by absorption with an aqueous regenerative solvent. There is a variety of treating processes available with the most common refinery operations based upon amine-based solvents.

- o Hydrotreating - Hydrotreating involves the catalytic conversion of organic nitrogen, sulfur, and oxygen compounds into hydrocarbons and the more readily removable sulfides, ammonia, and water. Various process streams normally are

treated separately because of various fuel specifications and the wide range of catalysts and reactor conditions required to hydrotreat the various petroleum fractions.

### Conversion

Conversion processes typically involve cracking, combination, and rearrangement.

#### o Cracking

Thermal Cracking - This is a relatively simplistic process which involves the heating of hydrocarbon fractions in the absence of catalysts. A modification to this traditional process, known as vis-breaking, is used to minimize coke formation. The moderate heating to 880°F is employed to reduce the feed viscosity and, therefore, reduce the quantity of blending stock required to upgrade the feed to fuel oil specifications. Delayed coking uses severe heating conditions (1800°F-2000°F) to crack feedstock to coke gas, distillates, and coke. Fluid coking is a recent innovation which converts the feed stream to higher valued products and produces less coke.

Hydrocracking - This process involves the cracking of feedstocks in the presence of a high hydrogen partial pressure. This process normally is employed on a high sulfur, straight-run gas or on a gas-oil effluent from another cracking process.

Catalytic Cracking - Catalytic cracking involves the application of catalytic reactions to reduce heavy oils maxi-

mizing production of light C<sub>4</sub> hydrocarbons and C<sub>5</sub> and C<sub>6</sub> gasoline compounds. This process is primarily employed to maximum gasoline production.

o Combination - These processes involve the combination of two light hydrocarbons through polymerization or alkylation to produce a gasoline-range hydrocarbon. The polymerization process combines two or more gaseous olefins into a liquid product, while the alkylation process joins an isoparaffin and olefin. The feedstock origin is either a catalytic or hydrocracker and the catalysts include phosphoric, sulfuric, or hydrofluoric acid.

o Rearrangement - This process involves the application of catalytic reforming and isomerization to rearrange the molecular structure of a feedstock to produce a high quality stream for gasoline blending.

Catalytic reformers create high octane naphthas (rich in benzene, toluene, and xylene) from a desulfurized, straight-run, or cracked naphtha. Hydrogen also may be produced as part of the reforming operation and other end-products, including non-aromatics.

Isomerization units are used to increase the octane ratings of pentane and hexane fractions to produce a gasoline-blending stock having an octane number of 80-85. The reaction is conducted at elevated temperatures (> 300°F) and pressure (400 psig) over a chlorinated-platinum-aluminum-oxide catalyst.

## Blending

The typical in-line blending operations most commonly involve the final processing of gasoline prior to storage. A variety of gasoline components, such as cracked gasoline, reformate, isomerate, alkylate, and butane, are combined with selective additives in the necessary proportions to meet marketing specifications.

## Auxiliary Operations

o Crude Desalting - This process involves the separation of inorganic salts and brines from an incoming crude to prevent process fouling, corrosion, and catalyst poisoning. The desalting process can be conducted either electrically or chemically with the former being the more prevalent. In the electric process, the raw crude is heated, emulsified with water, and routed through a high-voltage vessel where the electric field demulsifies the oil and water. In the chemical version of this process, coalescing agents are applied to demulsify the two-phase aqueous-organic system.

o Hydrogen Generation - Large quantities of hydrogen are consumed in numerous refinery operations, including hydrotreating, hydrocracking, and isomerization. The proper maintenance of a hydrogen balance within the typical refinery requires that the hydrogen available from the catalytic reformers be supplemented by either steam-hydrocarbon reforming or partial oxidation. The selection of either

process depends upon the characteristics of the raw feedstock material.

- o Sulfur Recovery - This process involves the application of specific processes, such as the Claus process, to convert the hydrogen sulfide content of acid gas to elemental sulfur. In this process, the hydrogen sulfide is combusted in an oxygen-deficient atmosphere to produce sulfur, sulfur dioxide, and water. Additional sulfur recovery is obtained in a series of catalytic reactors through reaction of hydrogen sulfide and sulfur dioxide. The tail gas from the Claus unit may be treated further through a variety of processes.

- o Power Generation - The major factor affecting power generation in refining operations is the requirement for steam and the overall facility steam balance. Facility requirements can range from a simple back-up boiler for operations where there are significant amounts of by-product steam to other situations where continuous steam generation is necessary.

#### Storage Technologies

- o No Storage - Raw material is not stored, but is pumped directly from an adjacent process area or petroleum refining facility where it is produced. This procedure is employed when the production in two process areas is integrated to the degree that simultaneous operations occur and no intermediate storage is necessary. Material transfer would occur by

pumping through steel or other piping from one process area directly to the other.

o Tank Storage

Fixed Roof - These cylindrical steel tanks have permanently attached conical steel roofs. The rigid construction of these tanks necessitates that the roof be installed with pressure-vacuum valves set at a few inches of water to contain minor vapor volume expansion. Greater losses of vapor resulting from tank filling should be controlled with an attached vapor recovery unit.

Floating Roof - Unlike fixed roof tanks, these tanks are equipped with a sliding roof that floats on the surface of the product and eliminates the vapor space between product and roof. A sliding seal attached to the roof seals the annular space between the roof and vessel wall from evaporation.

Internal Floating Cover - To remedy the problems of snow and rain accumulation encountered with floating roofs, this design utilizes both a fixed outer roof and an internal floating cover. Again, the floating cover is equipped with sliding seals to prevent annular space evaporation.

Variable Vapor Space - These tanks may appear in two basic designs: lifter roof and diaphragm. The lifter roof type utilizes a telescopic roof, free to travel up or down as the vapor space expands or contracts. The diaphragm design has an internal flexible diaphragm to accommodate vapor volume changes.

Pressure - These tanks are especially useful for storing highly volatile materials. These tanks come in a wide variety of shapes and are designed to eliminate vapor emissions by storing the product under pressure. These tanks may be designed for pressures up to 200 psi.

It has been noted that fixed roof, floating roof, and internal floating cover tanks are the most common varieties in use for storage of organic materials. These tanks may range in size from 20,000 to 500,000 bbl. and average 70,000 bbl.

## Attachment II

### SOLUBILITY AND ENVIRONMENTAL MOBILITY

### CHARACTERISTICS OF CHROMIUM COMPOUNDS

The tripositive state is the most stable form of chromium. In this state chromium forms strong complexes (coordination compounds) with a great variety of ligands such as water, ammonia, urea, halides, sulfates, amines and organic acids.(a,b) Thousands of such compounds exist. This complex formation underlies the tanning reactions of chromium, and is responsible for the strong binding of trivalent chromium by soil elements, particularly clays.(c,d)

At pH values greater than about 6, trivalent chromium forms high molecular weight, insoluble, "polynuclear" complexes of  $\text{Cr}(\text{OH})_3$  which ultimately precipitate as  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . This process is favored by heat, increased chromium concentration, salinity and time.(a) These chromium hydroxy complexes, formed during alkaline precipitation treatment of Cr-bearing wastes, are very stable, and relatively unreactive, because the water molecules are very tightly bound. In this form, Cr is therefore resistant to oxidation. Three acid or base catalyzed reactions are responsible for the solubilization of chromium hydroxide:

<u>Reaction</u>	<u>Keq. (18)</u>	<u>Cr(III) Concentration Calculated from keq (mg/l)</u>		
		<u>pH5</u>	<u>pH6</u>	<u>pH7</u>
1. $\text{Cr}(\text{OH})_3 + 2\text{H}^+ \rightleftharpoons \text{CrOH}^{++} + 2\text{H}_2\text{O}$	$10^8$	520	5.2	0.052
2. $\text{Cr}(\text{OH})_3 \rightleftharpoons \text{Cr}^{+3} + 3\text{OH}^-$	$6.7 \times 10^{-31}$	35	0.035	1*
3. $\text{Cr}(\text{OH}) \rightleftharpoons \text{H}^+ \text{CrO}_2^- + \text{H}_2\text{O}$	$9 \times 10^{-17}$	1	1	1

\*1= <0.001 mg/l

It is apparent from these figures that, in theory, trivalent chromium could leach from sludges to some extent. Such solubilized chromium, however, is unlikely to contaminate aquifers. It is complexed with soil materials, and tenasiously held.(a,d) Little soluble chromium is found in soils.(a,e) If soluble trivalent chromium is added to soils it rapidly disapperas from solution and is transformed into a form that is not extracted by ammonium acetate or complexing agents.(c,e) However, it is extractable by very strong acids, indicating the formation of insoluble hydroxides.(d,e) Thus: above pH5, chromium(III) is immobile because of precipitation; below pH4, chromium(III) is immobile because it is strongly absorbed by soil elements; between pH 4 and 5 the combination of absorpction and precipitation should render trivalent chromium quite immobile.(c,d)

In contrast, hexavalent chromium compounds are quite soluble, and hexavalent chromium is not as strongly bound to

soils.(c,d) Hexavalent chromium remains as such in a soluble form in soil for a short time, and is eventually reduced by reducing agents if present.(e,f) As compared with the trivalent form, hexavalent chromium is less strongly adsorbed and more readily leached from soils(d) and thus, is expected to have mobility in soil materials.(d)

## References

- a. U.S. EPA, Reviews of the Environmental Effects of Pollutants; III Chromium. ORNL/EIS-80; EPA-600/1-78-023; May 1980.
- b. Transition Metal Chemistry, R.L. Carlin, ed. Marcel Dekker, New York. 1965; Volume 1.
- c. Bartlett, R.J. and J.M. Kimble. Behavior of Chromium in Soils: I Trivalent Forms. J. Environ. Qual. 5: 379-383: 1976.
- d. Griffin, R.A., A.K. Au, and R.R. Frost. Effects of pH on adsorption of chromium from landfill leachate by clay minerals. J. Environ. Sci. Health A12(8): 430-449:1977.
- e. U.S. EPA. Application of Sewage Sludge to Cropland; Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals. EPA 430/9-76-013. NTIS PB No. 264-015. November, 1976.
- f. Bartlett, R.J. and J.M. Kimble. Behavior of Chromium in Soils: II Hexavalent Forms. Ibid. 5:383-386. 1976.

## **Iron and Steel Industry**

## LISTING BACKGROUND DOCUMENT

### COKING

#### Ammonia Still Lime Sludge (T)

##### I. Summary of Basis for Listing

Ammonia still lime sludge is generated when by-products are recovered from coke oven gases. The Administrator has determined that ammonia still lime sludge may pose a present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. These sludges contain the hazardous constituents cyanide, naphthalene, phenolic compounds, and arsenic which adhere to the lime flocs and solids in significant concentrations.
2. Cyanide and phenol leached in significant concentrations from an ammonia still lime sludge waste sample which was tested by a distilled water extraction procedure. Although no leachate data is currently available for naphthalene and arsenic, the Agency strongly believes that based on constituent solubilities, the high concentration of these constituents in the wastes, and the physical nature of the waste, these two constituents are likely to leach from the wastes in harmful concentrations when the wastes are improperly managed.
3. It is estimated that a very large quantity, 963,000 tons (1), of ammonia still lime sludge (5% solids by weight) is currently generated annually, and that this quantity will gradually increase to 1.45 million tons (5% solids by weight) per year as the remaining coke plants add fixed ammonia removal capability to comply with BPT limitations (1). There is thus the likelihood of large-scale contamination of the environment if these wastes are not managed properly.
4. Coke plant operators generally dispose of these sludges on-site in unlined sludge lagoons or in unsecured land-fill operations. These management methods may be in-

adequate to impede leachate migration\*.

## II. Industry Profile and Process Description

The stripping of ammonia during the by-product cokemaking process is currently practiced at 39 facilities, distributed across 17 different states, with about half of the operating plants located in Pennsylvania, Ohio and Alabama (1). These plants are currently producing 45,000,000 tons of coke per year (1). (Coke, the residue from the destructive distillation of coal, serves both as a fuel and as a reducing agent in the making of iron and steel.) Of the 39 plants which practice ammonia recovery, 31 use lime, generating, in the process, an ammonia still lime sludge.\*\*

During the recovery of chemical by-products from the cokemaking process, excess ammonia liquor is passed through stills to strip the  $\text{NH}_3$  from solution for recovery as ammonium sulfate, phosphate or hydroxide. About half of the ammonia originally present (5,000 mg/l) strips readily, but the remaining fraction can only be recovered by elevating the pH

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\*Although no data on the corrosivity of ammonia still lime sludge are currently available, the Agency believes that these sludges may have a pH greater than 12.5 and may, therefore, be corrosive. Under §262.11, generators of this waste stream are responsible for evaluating their waste in order to determine whether their waste is corrosive.

\*\*Eight plants currently use sodium hydroxide as their alkali and produce about 1/5 of the sludge volumes common to lime systems (1). These eight plants tend to be smaller in capacity, with lesser volumes of process wastewater to treat. The Agency believes that this sludge will be similar in composition to the ammonia still lime sludge, and plans on collecting additional data to determine whether this waste should also be listed.

of the waste liquor to 10-12 through the addition of lime, and passing additional steam through the solution. This stripping transfers some of the contaminants to the gas stream, but enough remains behind for the lime sludges to contain high levels of hazardous constituents (i.e., cyanide, naphthalene, phenol and arsenic; see page 6, following).

## II. Waste Generation and Management

Ammonia still lime sludge is generated in the recovery of ammonia, by the addition of lime, from coke manufacturing operations. Currently it is estimated that 963,000 tons of ammonia still lime sludges (5% solids by weight) are generated annually, and this amount will gradually increase to about 1.45 million tons per year as the remaining coke plants add fixed ammonia removal capabilities to comply with BPT limitations (1). Based on process wastewater analytical data at 9 coke-making plants, an estimated industry total of 1,468 tons (dry weight) of cyanide, naphthalene, phenolic compounds, and arsenic result each year from ammonia still lime sludges (1).

Cyanide, naphthalene, phenol and other organic constituents are formed as a result of the destructive distillation of coal and are present in the ammonia liquor. Arsenic, on the other hand, is present along with other naturally occurring metallic contaminants in the coal and is also present in the ammonia liquor. (Although other metals are present in the waste, only arsenic is deemed present in sufficient concen-

trations to present a problem (1).)

Review of the chemical mechanisms, pH and operating temperatures at which the ammonia stripping process is conducted indicates that cyanide, naphthalene, phenol and arsenic tend to remain relatively chemically unreactive in the ammonia still stripping process. As a result, the presence of these four pollutants in the ammonia still lime sludge is predictable.

Sludges are typically settled out in sedimentation basins, from which settled material is periodically removed for disposal (1). Figure 1 presents a process schematic of the ammonia still recovery process.

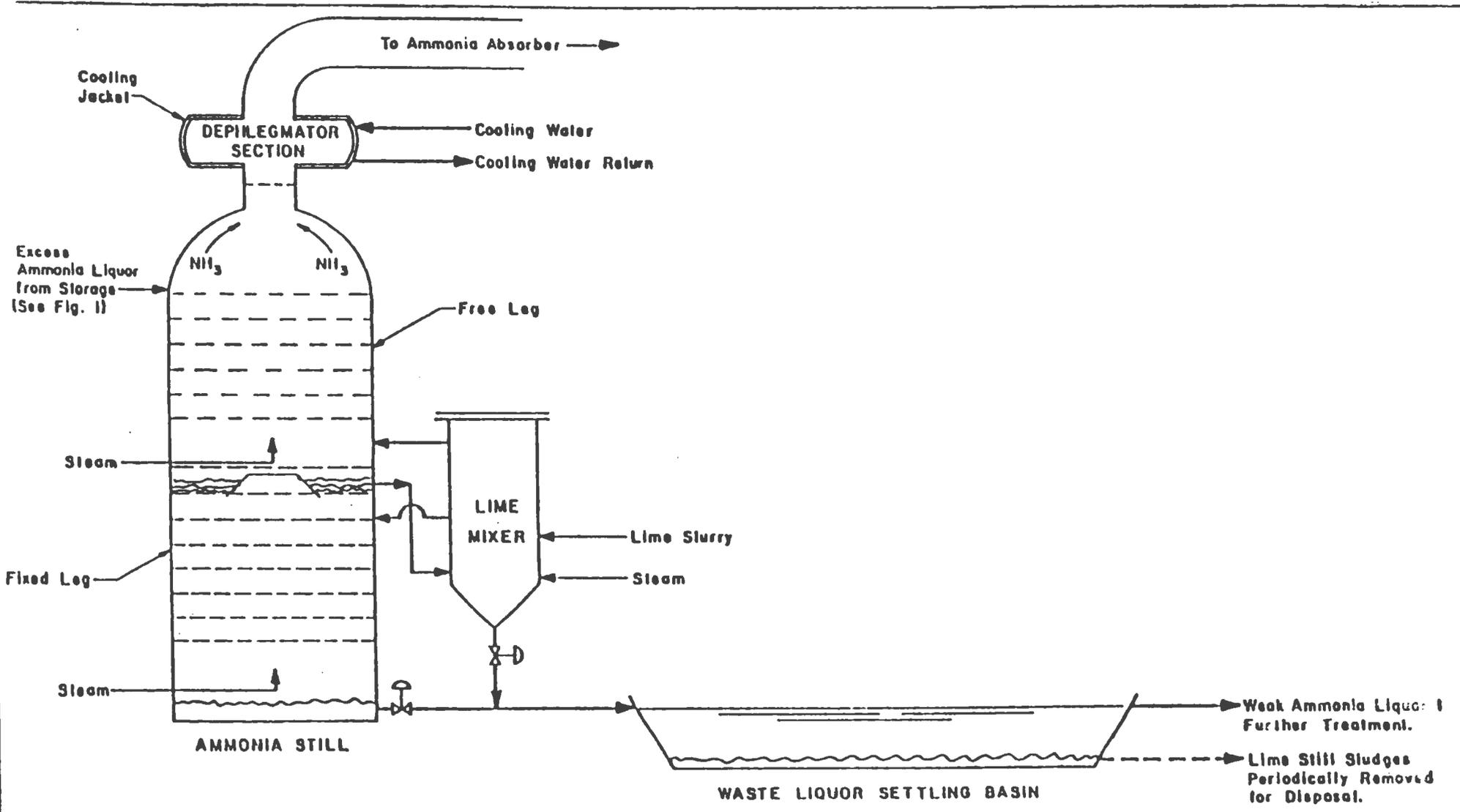
#### Current Disposal Practices

Of the 39 ammonia recovery operations, approximately 30 plants presently dispose of the ammonia still lime sludges in on-site unlined sludge ponds.(1) Lined lagoons or carefully controlled landfills have not been routinely used by the industry to dispose of these sludges (1).

#### Hazardous Properties of the Waste

Using data collected by EPA at coking operations from the process wastewater samples taken before and after the addition of lime(1), an accounting of the differences in pollutant mass before and after the lime addition reveals that 13,640 ppm of cyanide, 4,770 ppm naphthalene, 680 ppm of phenols\*, and 1,086

\*The mass of phenolic compounds present in the sludge is estimated and has been adjusted for partial volatilization of the phenol in the stripper.



-----> Hazardous Waste Source  
Requiring Controlled Disposal

ENVIRONMENTAL PROTECTION AGENCY		
STEEL INDUSTRY STUDY		
BY-PRODUCT COKEMAKING OPERATION		
HAZARDOUS WASTE SOURCE		
AMMONIA STILL LIME SLUDGES		
		FIGURE

ppm of arsenic are present in the ammonia still lime sludge.\*

A separate study of ammonia still lime sludge indicated phenol and cyanide concentrations ranging from 670 ppm to 1910 ppm for phenol and 343 ppm to 1940 ppm for cyanide (?).

Leaching tests (distilled water) were also performed on this waste sample. Results of these test revealed leachate concentrations of 198 ppm for cyanide and 20 ppm for phenol (2).

The concentration of cyanide in the leachate is far in excess of concentrations in water considered harmful to human health and the environment. For example, the U.S. Public Health Service's recommended standard for cyanide in drinking water is 0.2 mg/l. The proposed EPA Water Quality Criteria limits the level of cyanide at 0.2 mg/l and phenol at 1 ppm for domestic water supply.\*\*

Although no leachate data is currently available for naphthalene and arsenic, the Agency strongly believes that these constituents will leach in harmful concentrations from these wastes if not properly managed. Some compounds of arsenic are quite soluble. Arsenic trioxide has a solubility of 12,000 mg/l at 0°C, and arsenic pentoxide has a solubility of 2,300 g/l at 20°C (Appendix A). The solubility, the high concentrations

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\*These concentration figures are not contained in reference 1 but are calculated using data contained in that reference.

\*\*The Agency is not using these standards as quantitative benchmarks, but is citing them to give some indication that very low concentrations of these contaminants may give rise to a substantial hazard.

of arsenic in the ammonia still lime sludge and arsenic's extreme toxicity make it likely that it will leach from the wastes in harmful concentrations (i.e., a small quantity of arsenic is sufficient to present a problem to human health and the environment) if the wastes are not properly managed. Naphthalene is water soluble, with solubility ranging from 30,000 g/l to 40,000 g/l. The solubility of naphthalene in water and its presence in such high concentrations in the waste make it likely that it will also leach from the waste in harmful concentrations if the wastes are not properly managed.

In addition, cyanide, phenol, naphthalene and arsenic tend to remain chemically unreactive in the ammonia still lime sludge. Since lime is a relatively porous substance, constituents in the lime sludge will themselves therefore tend to be released when the waste sludge is exposed to a leaching medium.

As previously discussed, a very large quantity of ammonia still lime sludge is produced annually, and is thus available for large scale contamination of the environment. Such large quantities of waste likewise present the danger of continued migration of and exposure to waste constituents. These wastes consequently present a serious hazard to human beings if not properly managed.

Current practices of disposing of these wastes in fact appear inadequate. Disposal of ammonia still lime sludge in unlined sludge lagoons or unsecured landfills (see p. 4 above)

makes it likely that the hazardous constituents in the wastes will leach out and migrate into the environment, possibly contaminating drinking water sources.

An overflow problem might also be encountered if the liquid portion of the waste has been allowed to reach too high a level in the lagoon; a heavy rainfall could cause flooding which might result in the contamination of surface waters in the vicinity. Given the large quantities of this waste produced, other types of mismanagement are likely to result and to cause damage to the environment.

As demonstrated above, the waste constituents appear capable of migrating from the waste in harmful concentrations. The waste constituents are also persistent, and thus have an increased likelihood of reaching an environmental receptor. Arsenic, as an element will persist indefinitely in some form. Cyanides also tend to persist after migration (see background document "Spent or Waste Cyanide Solutions and Sludges" for further information supporting this conclusion). Cyanide and phenols have been implicated in actual damage incidents as well, again confirming the ability of these waste constituents to be mobile, persist, and cause substantial harm. For example,

A firm in Houston, Texas, as early as 1968, was made aware that its practices of discharging such hazardous wastes as cyanide, phenols, sulfides, and ammonia into the Houston Ship Channel was creating a severe environmental hazard. The toxic wastes in question were derived from the cleaning of blast furnaces from coke plants. According to expert testimony, levels as low as 0.05 mg/l of cyanide effluent are lethal to shrimp and small fish. The court ordered the firm to cease discharging these wastes into the ship channel. (EPA open files)

In 1971 a newly drilled industrial well in an artesian aquifer in Garfield, New Jersey, contained water with an unacceptably high concentration of phenolic materials. The pollutants originated from nearby industrial waste lagoons. (Draft Environmental Impact Statement, January, 1979).

Fifteen thousand drums of toxic and corrosive metal industrial wastes were dumped on farmland in Illinois in 1972. As a result, large numbers of cattle died from cyanide poisoning and nearby surface water was contaminated by runoff. (House Report Number 94-1491, 94th Congress, 2nd Session, page 19).

## Health and Ecological Effects

### Cyanide

“ Congress listed cyanide as a priority pollutant under §307(a) of the Clean Water Act.

The toxicity of cyanide has been well documented. Cyanide in its most toxic form can be fatal to humans in a few minutes at a concentration of 300 ppm. Cyanide is also lethal to freshwater fish at concentrations as low as about 50 mg/l and has been shown to adversely affect invertebrates and fish at concentrations of about 10 mg/l.

The hazards associated with exposure to cyanide have also been recognized by other regulatory programs. The U.S. Public Health Service established a drinking water standard of 0.2 mg/l as an acceptable level for water supplies. The Occupational Safety and Health Administration (OSHA) has established a permissible exposure limit for KCN and NaCN at 5 mg/m<sup>3</sup> as an eight-hour time-weighted average.

Finally, final or proposed regulations of the states of California, Maine, Maryland, Massachusetts, Minnesota, Missouri,

New Mexico, Oklahoma, and Oregon define cyanide containing compounds as hazardous wastes or components thereof. Additional information and specific references on the adverse health effects of cyanide can be found in Appendix A.

### Phenol

Congress designated phenol a priority pollutant under §307(a) of the Clean Water Act. Phenol is readily absorbed by all routes. It is rapidly distributed to mammalian tissues. This is illustrated by the fact that acutely toxic doses of phenol can produce symptoms within minutes of administration regardless of the route of entry. Repeated exposures to phenol at high concentrations have resulted in chronic liver damage in humans.<sup>(3)</sup> Chronic poisoning, following prolonged exposures to low concentrations of the vapor or mist, results in digestive disturbances (vomiting, difficulty in swallowing, excessive salivation, diarrhea), nervous disorders (headache, fainting, dizziness, mental disturbances), and skin eruptions.<sup>(4)</sup> Chronic poisoning may terminate fatally in some cases where there has been extensive damage to the kidneys or liver.

Phenol biodegrades at a moderate rate in surface water and soil, but moves readily. Even with persistence of only a few days, the rapid spreading of phenol could cause widespread damage of the ecosystem and contamination of potable water supplies.

OSHA has set a TLV for phenol at 5 ppm.

Phenol is listed in Sax's Dangerous Properties of Industrial Materials as a dangerous disaster hazard because

when heated it emits toxic fumes. Additional information and specific references on the adverse effects of phenol can be found in Appendix A.

### Arsenic

Congress has designated arsenic as a priority pollutant under Section 307(a) of the Clean Water Act.

Arsenic is extremely toxic in humans and animals. Death in humans has occurred following ingestion of very small amounts (5mg/kg) of this chemical. Several epidemiological studies have associated cancers with occupational exposure to arsenic, including those of the lung, lymphatics and blood. Certain cases involving a high prevalence of skin cancer have been associated with arsenic in drinking water, while liver cancer has developed in several cases following ingestion of arsenic. Results from the administration of arsenic in drinking water or by injection in animals supports the carcinogenic potential of arsenic.

Occupational exposure to arsenic has resulted in chromosomal damage, while several different arsenic compounds have demonstrated positive mutagenic effects in laboratory studies.

The teratogenicity of arsenic and arsenic compounds is well established and includes defects of the skull, brain, gonads, eyes, ribs and genito-urinary system.

The effects of chronic arsenic exposure include skin diseases progressing to gangrene, liver damage, neurological

disturbances, red blood cell production, and cardiovascular disease.

OSHA has set a standard air TWA of 500 mg/m<sup>3</sup> for arsenic. DOT requires a "poision" warning label.

The Office of Toxic Substances under FIFRA has issued a pre-RPAR for arsenic. The Carcinogen Assessment Group has evaluated arsenic and has determined that it exhibits substantial evidence of carcinogenicity. The Office of Drinking Water has regulated arsenic under the Safe Drinking Water Act due to its toxicity and the Office of Air Quality Planning and Standards has begun a pre-regulatory assessment of arsenic based on its suspected carcinogenic effects. The Office of Water Planning and Standards under Section 304(a) of the Clean Water Act has begun development of a regulation based on health effects other than on oncogenicity and environmental effects. Finally, the Office of Toxic Substances has completed Phase I assessment of arsenic under TSCA. Additional information and specific references on the adverse effects of arsenic can be found in Appendix A.

### Naphthalene

Naphthalene is designated a priority pollutant under Section 307(a) of the CWA.

Systemic reaction to acute exposure to naphthalene includes nausea, headache, diaphoresis, hematuria, fever, anemia, liver damage, convulsions and coma. Industrial exposure to naphthalene appears to cause increased incidence of cataracts. Also, hemolytic anemia with associated

jaundice and occasionally renal disease from precipitated hemoglobin has been described in newborn infants, children, and adults after exposure to naphthalene by ingestion, inhalation, or possibly by skin contact.

OSHA's standard for exposure to vapor for a time-weighted industrial exposure is 50 mg/m<sup>3</sup>.

Sax<sup>(10)</sup> warns that naphthalene is an experimental neoplastic substance via the subcutaneous route; that is, it causes formation of non-metastasizing abnormal or new growth(s). Additional information and specific references on the adverse effects of naphthalene can be found in Appendix A.

## References

1. U.S EPA. Draft development document for proposed effluent limitations guidelines and standards for the iron and steel manufacturing point source category; by-product cokemaking subcategory, V.II, October, 1979. EPA No. 440/1-79-024a. 1979.
2. Calspan Corporation. Assessment of industrial hazardous waste practices in the metal smelting and refining industry. Appendices 12,37. Contract Number 68-01-2604, Volume III, pages 97-144. NTIS PB No. 276 171. April, 1977.
3. Merliss, R.R. Phenol Moras. Mus. Jour. Occup. Med. 14:55. 1972.
4. Sax, N. Irving. Dangerous properties of industrial materials, 5th ed. Van Nostrand Reinhold Co., New York. 1979.

## LISTING BACKGROUND DOCUMENT

### ELECTRIC FURNACE PRODUCTION OF STEEL

Emission control dusts/sludges from the primary production of steel in electric furnaces (T)\*

#### Summary of Basis for Listing

Emission control dusts/sludges from the primary production of steel in electric furnaces are generated when particulate matter in the gases given off by electric furnaces during the production process is removed by air pollution control equipment. Dry collection methods generate a dust; wet collection methods generate a sludge. The Administrator has determined that these dusts/sludges are solid wastes which may pose a present or potential hazard to human health and the environment when improperly transported, treated, stored, disposed of or otherwise managed and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- (1) The emission control dusts/sludges contain significant concentrations of the toxic metals chromium, lead, and cadmium.
- (2) Lead, chromium and cadmium have been shown to leach in harmful concentrations from waste samples subjected to both a distilled water extraction procedure and the extraction procedure described in §250.13(d) of the proposed Subtitle C regulations.

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\*This listing was originally proposed on December 18, 1978 (43 FR 58959) under SIC Code 3312 and states as "Iron Making: Electric furnace dust and sludge." In response to a comment submitted by the American Iron and Steel Institute that the electric furnace process is used for steelmaking only, not iron and steelmaking as was previously listed, the Agency modified the listing on May 19, 1980 (45 FR 33124) as "Emission control dusts/sludges from the electric furnace production of steel." In further response to a comment submitted by the American Foundryman's Society, the Agency is again modifying the listing to make it clear that this listing is meant to apply to primarily steel producers only (see Response to Comments in back of this document for more detailed discussion).

- (3) A large quantity of these wastes (a combined total of approximately 337,000 metric tons) is generated annually and is available for disposal. There is thus a likelihood of large scale contamination of the environment if these wastes are mismanaged.
- (4) The wastes typically are disposed of by being dumped in the open, either on-site or off-site, thus posing a realistic possibility of migration of lead, cadmium, and chromium to underground drinking water sources. These metals persist virtually indefinitely, presenting the serious threat of long-term contamination.
- (5) Off-site disposal of these wastes will increase the risk of mismanagement during transport.

#### I. Profile of the Industry

The electric furnace (arc) process is one of the three principal methods of producing steel in the United States. In 1974, the iron and steel industry had the capacity to produce approximately 27,000,000 metric tons/year of steel via the electric furnace process (1).

Plants are located in 31 different states, with 70% of the estimated capacity located in Ohio, Pennsylvania, Illinois, Texas, Michigan and Indiana (1). A typical integrated electric furnace steel plant has an electric furnace capacity of about 500,000 metric tons/yr (1). Capacities at different plants range from about 50,000 to 2,000,000 metric tons/yr (2).

#### II. Manufacturing Process

The raw materials for the electric arc steelmaking process include cold iron and steel scrap, and fluxes such as limestone and/or fluorspar. The raw materials are charged into a refractory-lined cylindrical furnace and melted by

passing an electric current (arcing) through the scrap steel by means of three triangularly spaced carbon electrodes inserted through the furnace roof. The process proceeds at high temperatures and an oxidizing atmosphere (air or pure oxygen are used).(2) The electrodes are consumed at a rate of about 5 to 8 kg/kkg of steel, with the emission of CO and CO<sub>2</sub> gases. The hot gases entrain finely divided particulate, 70% of which (by weight) are less than 5 microns in size, the majority of this less than 0.5 microns. The particulate fume or dust consists primarily of iron oxides, silica and lime, with significant concentrations of the toxic metals lead, chromium and cadmium (1).

### III. Waste Generation

The waste products from the electric carbon furnace process is a mixture of gases consisting of smoke, slag, carbon, nitrogen, ozone and oxides of iron as well as other metals. (2) The particulates produced during the electric furnace steelmaking process are removed from the furnace off-gases by means of baghouse filters, electrostatic precipitators, or high-energy Venturi scrubbers. The baghouse filters and electrostatic precipitators, which are used by 93% of electric arc steelmaking furnaces, produce an emission control (dry) dust for disposal at a rate of 12.8 kg of dust per metric ton of steel produced. Scrubbers, used by the remaining 7% of the steelmaking industry, produce slurries or sludges for disposal at a rate of about 8.7 kg (dry solids

basis) per metric ton of steel produced.

Based on an electric furnace steelmaking capacity of 27,000,000 kkg/yr (see p. 2 above), and assuming that the electric furnaces that use dry air pollution control equipment represent 93% of that capacity, the industry-wide estimated quantities of emission control dusts and sludges produced at full operating capacity are 321,000 kkg/yr, and 16,000 kkg/yr (dry solids basis), respectively.

The Agency has information indicating that these wastes are typically dumped in the open at on-site or off-site disposal facilities (1,2). The emission control sludges, however, are also amenable to other forms of disposal, such as disposal in lagoons or surface impoundments. The large quantities of these wastes generated annually, combined with the fact that other emission control dusts/sludges generators handle their wastes in this manner, make this type of management situation plausible. (See, for example, Secondary Lead Hazardous Waste Listing Background Document).

#### IV. Hazardous Properties of the Wastes

##### 1. Migrating Potential of Waste Constituents

An analysis of the electric furnace dust supplied by U.S. Steel Corporation is given in Table 1 (3). As the data indicate, two of the toxic metals of concern, lead and chromium, are present in significant concentrations. Lead, for example, which has a usual range of lead-in-soil concentrations of 2

to 200 ppm (4), is present in this waste sample at a concentration of 1,400 ppm.\*

Another analysis of waste samples from both electric furnace dusts and sludges also shows lead and chromium to be present in the wastes in significant amounts. The analysis of the emission control dust waste sample revealed chromium to be present at 1380 ppm and lead to be present at 24,220 ppm. The analysis of the emission control sludge sample revealed total chromium to be present in the waste at 2,690 ppm and lead at 7,900 ppm (1).

The metal oxide particulates in these dusts are formed at high temperatures in an oxidizing atmosphere. Such conditions are known to result in the oxidation of chromium to its hexavalent form.<sup>(16)</sup> The dusts and sludges, therefore, are presumed to contain hexavalent chromium compounds.

The presence of such high concentrations of lead and (presumably hexavalent) chromium in this waste stream, in and of itself, raises regulatory concerns. Furthermore, the Agency has data (see table 2, p. 8) from the proposed EPA Extraction Procedures (Samples 1-4) and an industry-conducted water extraction (Sample 5) which show that lead, chromium and cadmium may

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\*The absence of cadmium from the waste sample described in Table 1 may be attributable to the fact that 29% of the constituents (by weight) of the waste sample are not accounted for, or the fact that the composition of electric furnace dust can vary considerably depending on the type and quantity of cold scrap used to charge the furnace. Cadmium is a demonstrated waste constituent as evidenced by its presence in significant concentrations in the leachate tests on electric furnace dusts shown in Table 2 below.

Table 1

## Composition of an Electric Furnace Dust\*

<u>Parameter</u>	<u>Weight %</u> (not intended to total 100%)
Fe (total)	35.34
MnO	8.29
SiO <sub>2</sub>	5.61
Al <sub>2</sub> O <sub>3</sub>	0.62
CaO	12.01
Cr <sub>2</sub> O <sub>3</sub>	2.69
CuO	0.12
Ni	0.59
Pb	0.14
Zn	0.39
F	<u>5.09</u>
Total	70.89

Source: Reference 3

\*Although the data in Table 1 is presented for the electric furnace dusts collected by baghouse filters or electric precipitators and not for the sludges produced by Venturi scrubbers, the solids composition of the sludges produced by scrubbers can be assumed to be virtually the same as that of the electric furnace dusts since both wet and dry air pollution systems entrain the same heavy metal particulate.

leach from electric furnace dusts in significant concentrations. In view of the relative insolubility of trivalent chromium (see Attachment I), the demonstrated leaching of chromium in these tests points to the probable presence in these wastes of hexavalent chromium. All of the waste extracts--either by the EPA EP procedure which uses acetic acid as its leaching solution, or by the industry test which uses distilled water--contain contaminants in concentrations which are either equal to or, for the most part, exceed EPA's National Interim Primary Drinking Water Standards, in some instances by several orders of magnitude. The distilled water extraction shown in Sample 5 of Table 2 indicates that these wastes may leach harmful concentrations of lead, cadmium, and (presumably hexavalent) chromium even under relatively mild conditions.

This conclusion is further supported by different solubility tests done on electric furnace emission control dust waste samples, also using water as the leaching medium (1). In this test, lead was again found to leach at dangerous concentrations, e.g. 150 ppm. Another water solubility test done on an electric furnace sludge waste sample likewise showed chromium and lead to leach from the sludge in significant concentrations of 94 ppm and 2.0 ppm, respectively (1).

If these wastes are exposed to more acidic environments (landfills or disposal environments subject to acid rainfall) these metals' concentrations in leachate would likely be higher, since most compounds of lead, cadmium, and chromium are more soluble in acid than in distilled water (5,6,7).

Table 2.

Leach Test Results (mg/l) on Electric Furnace Emission Dusts

<u>Contaminant</u>	<u>National Interim Primary Drinking Water Standard</u>	<u>Sample 1*</u>	<u>Sample 2*</u>	<u>Sample 3*</u>	<u>Sample 4*</u>	<u>Sample 5**</u>	<u>Sample 6***</u>
Cd	0.01	0.05	2.84	3.85	4.8-13.4	3.5	-
Cr	0.05	<0.1	0.48	-	0.05	1,248.0	120.0
Pb	0.05	0.5	0.06	36.7	<0.2	0.3	.16

\*EP extraction data submitted by an American Iron and Steel Institute letter to John P. Lehman from Earle F. Young, Jr., dated May 15, 1979.

\*\*Waste Characterization Data for the State of Pennsylvania, Department of Environmental Resources. The data for Sample 5 was supplied by Allegheny Ludlum Steel Corporation from a water extraction procedure. The apparent discrepancy between the result obtained for chromium in Sample 5 and those obtained for chromium in Samples 1-4 may be attributable to the particular type and quantity of scrap metal used in the steelmaking processes which produced these waste samples.

\*\*\*Source: Reference 3 water extraction.

Many of the states in which the majority of these wastes are generated, including Ohio, Pennsylvania, Illinois and Indiana, are known to experience acid rainfall (8).

A further indication of the migratory potential of the waste constituents is the physical form of the waste itself. These waste dusts/sludges are of a fine particulate composition, thereby exposing a large surface area to any percolating medium, and increasing the probability for leaching of hazardous constituents from the waste to groundwater.

## 2. Substantial Hazard from Waste Mismanagement

In light of the demonstrated migratory potential of harmful concentrations of the waste constituents, improper management of these wastes could easily result in the release of contaminants. For instance, selection of disposal sites in areas with permeable soils can permit contaminant-bearing leachate from the waste to migrate to surface water and/or groundwater. The possibility of groundwater contamination is especially significant with respect to disposal of these wastes in surface impoundments, since a large quantity of liquid is available to percolate through the solids and soil beneath the fill.

An overflow problem might also be encountered if these wastes are ponded and the liquid portion of the waste has been allowed to reach too high a level in the lagoon; a heavy rainfall could cause flooding which might result in the contamination of soils and surface waters in the vicinity.

In addition to difficulties caused by improper site selection, unsecure landfills in which dusts and dredged solids could be disposed of are likely to have insufficient leachate control practices. There may be no leachate collection or treatment system to diminish leachate percolation through the wastes and soil underneath the site to groundwater and there may not be a surface run-off diversion system to prevent contaminants from being carried from the disposal site to nearby surface waters.

In addition to ground and surface water contamination, airborne exposure to lead, chromium, or cadmium particulate escaping from mismanaged emission control dusts is another pathway of concern. These minute particles could be dispersed by wind if waste dusts are piled in the open, placed in unsecure landfills or improperly handled during transportation. As a result, the health of persons who inhale the airborne particulates would be jeopardized. This is especially true for hexavalent chromium compounds, whose carcinogenicity via inhalation is especially well substantiated.

Transportation of these wastes to off-site disposal facilities increases the likelihood of their causing harm to human beings and the environment. The mismanagement of these wastes during transportation may thus result in an additional hazard. Furthermore, absent proper management safeguards, the wastes might not reach the designated destination at all, thus making them available to do harm elsewhere.

The lead chromium and cadmium that may migrate from the waste to the environment as a result of such improper disposal practices are elemental metals that persist indefinitely in the environment in some form. Therefore, contaminants migrating from these wastes may pollute the environment for long periods of time.

### 3. Justification for T Listing

The Agency has determined to list emission control dusts/sludges from the primary production of steel in electric furnaces as a T hazardous waste on the basis of lead, chromium and cadmium constituents, although these constituents are also measurable by the E toxicity characteristic. Although concentrations of these constituents in an EP extract from waste streams from particular sites may not always be greater than 100 times the National Interim Primary Drinking Water Standards, the Agency believes that there are factors in addition to metal concentrations in leachate which justify the T listing. Some of these factors have already been identified, namely the high concentrations of cadmium, chromium and lead in the actual waste and in leachate samples, the non-degradability of these substances, and the strong possibility of the lack of proper management of the wastes in actual practice.

The quantity of these wastes generated is an additional supporting factor. As indicated above, electric furnace emission control dusts/sludges are generated in very substantial quantities, and contain high concentrations of the

toxic metals lead, chromium and cadmium. Large amounts of each of these metals are available for environmental release. The large quantities of these contaminants pose the danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time, since large amounts of pollutants are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or used up due to the large quantities of pollutant available. All of these considerations increase the possibility of exposure to the harmful constituents in the wastes, and in the Agency's view, support a T listing.

V. Hazards Associated with Lead, Chromium, and Cadmium

Lead is poisonous in all forms. It is one of the most hazardous of the toxic metals because it accumulates in many organisms, and its deleterious effects are numerous and severe. Lead may enter the human system through inhalation, ingestion or skin contact. Hexavalent chromium is toxic to man and lower forms of aquatic life. Cadmium is also a cumulative poison, essentially irreversible in effect. Excessive intake leads to kidney damage, and inhalation of dusts also damages the lungs. Additional information on the adverse health effects of lead, chromium, and cadmium can be found in Appendix A.

The hazards associated with exposure to lead, chromium, and cadmium have been recognized by other regulatory programs.

Lead, chromium and cadmium are listed as priority pollutants in accordance with §307(a) of the Clean Water Act of 1977. Under §6 of the Occupational Safety and Health Act of 1970, a final standard for occupational exposure to lead has been established and a draft technical standard for chromium has been developed (9, 10). Also, a national ambient air quality standard for lead has been announced by EPA pursuant to the Clean Air Act (9). In addition, final or proposed regulations of the State of California, Maine, Massachusetts, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define chromium and lead containing compounds as hazardous wastes or components thereof (11).

EPA has proposed regulations that will limit the amount of cadmium in municipal sludge which can be landspread on cropland (12). The Occupational Safety and Health Administration (OSHA) has issued an advance notice of proposed rulemaking for cadmium air exposure based on a recommendation by the National Institute for Occupational Safety (13). EPA has also prohibited the ocean dumping of cadmium and cadmium compounds except when present as trace contaminants (14). EPA has also promulgated pretreatment standards for electroplaters which specifically limit discharges of cadmium to Public Owned Treatment Works (15).

## References

1. U.S. EPA. Office of Solid Waste. Assessment of hazardous waste practices in the metal smelting and refining industry. v.3. EPA No. 8w-145c3. NTIS PB No. 276 179. April, 1977.
2. U.S. EPA. Development document for proposed effluent limitations guidelines and standards for the iron and steel manufacturing point source category, v.5. EPA No. 440/1-79/024a. October, 1979.
3. Waste Characterization Data from the State of Pennsylvania Department of Environmental Resources; letter from P.Y. Masciantonio to T. Orlando, dated September 8, 1975.
4. U.S. EPA. Quality criteria for water. Washington, D.C. 1976.
5. CRC Handbook of Chemistry and Physics, 52nd ed. The Chemical Rubber Company, Cleveland, Ohio. 1971-72.
6. The Merck Index, 8th ed. Merck & Co., Inc., Rahway, N.J. 1968.
7. Pourbaix, M. Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, London. 1966.
8. Not used in text.
9. U.S. Department of Interior, Bureau of Mines. Mineral commodity summaries, 1979.
10. NIOSH. Registry of toxic effects of chemical substances. U.S. Department of Health, Education and Welfare, National Institute for Occupational Safety and Health. 1977.
11. U.S. EPA State Regulations Files. Hazardous Waste State Programs, Wh-565, U.S. EPA, 401 M St., S.W., Washington, D.C. 20460. Contact Sam Morekas. (202) 755-9145.
12. 44 FR 53449.
13. 42 FR 5434.
14. 38 FR 28610.
15. Federal Register. Vol. 44. No. 175. Friday, September 7, 1979. (40 CFR Part 413).

## Attachment I

### SOLUBILITY AND ENVIRONMENTAL MOBILITY

### CHARACTERISTICS OF CHROMIUM COMPOUNDS

The tripositive state is the most stable form of chromium. In this state chromium forms strong complexes (coordination compounds) with a great variety of ligands such as water, ammonia, urea, halides, sulfates, amines and organic acids. (a,b) Thousands of such compounds exist. This complex formation underlies the tanning reactions of chromium, and is responsible for the strong binding of trivalent chromium by soil elements, particularly clays. (c,d)

At pH values greater than about 6, trivalent chromium forms high molecular weight, insoluble, "polynuclear" complexes of  $\text{Cr}(\text{OH})_3$  which ultimately precipitate as  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . This process is favored by heat, increased chromium concentration, salinity and time. (a) These chromium hydroxy complexes, formed during alkaline precipitation treatment of Cr-bearing wastes, are very stable, and relatively unreactive, because the water molecules are very tightly bound. In this form, Cr is therefore resistant to oxidation. Three acid or base catalyzed reactions are responsible for the solubilization of chromium hydroxide:

<u>Reaction</u>	<u>Keq. (18)</u>	<u>Cr(III) Concentration Calculated from keq (mg/l)</u>		
		<u>pH5</u>	<u>pH6</u>	<u>pH7</u>
1. $\text{Cr(OH)}_3 + 2\text{H}^+ \rightleftharpoons \text{CrOH}^{2+} + 2\text{H}_2\text{O}$	$10^8$	520	5.2	0.052
2. $\text{Cr(OH)}_3 \rightleftharpoons \text{Cr}^{3+} + 3\text{OH}^-$	$6.7 \times 10^{-31}$	35	0.035	1*
3. $\text{Cr(OH)}_3 \rightleftharpoons \text{H}^+ + \text{CrO}_2^- + \text{H}_2\text{O}$	$9 \times 10^{-17}$	1	1	1

\*1= <0.001 mg/l

It is apparent from these figures that, in theory, trivalent chromium could leach from sludges to some extent. Such solubilized chromium, however, is unlikely to contaminate aquifers. It is complexed with soil materials, and tenaciously held. (a,d) Little soluble chromium is found in soils. (a,e) If soluble trivalent chromium is added to soils it rapidly disappears from solution and is transformed into a form that is not extracted by ammonium acetate or complexing agents. (c,e) However, it is extractable by very strong acids, indicating the formation of insoluble hydroxides. (d,e) Thus: above pH5, chromium(III) is immobile because of precipitation; below pH4, chromium(III) is immobile because it is strongly absorbed by soil elements; between pH 4 and 5 the combination of absorption and precipitation should render trivalent chromium quite immobile. (c,d)

In contrast, hexavalent chromium compounds are quite soluble, and hexavalent chromium is not as strongly bound to

soils.(c,d) Hexavalent chromium remains as such in a soluble form in soil for a short time, and is eventually reduced by reducing agents if present.(e,f) As compared with the trivalent form, hexavalent chromium is less strongly adsorbed and more readily leached from soils(d) and thus, is expected to have mobility in soil materials.(d)

Response to Comments-Emission Control Dust/Sludge from the  
Electric Furnace Production of Steel

One commenter requested a clarification on the scope of waste K061 (Emission control dust/sludge from the electric furnace production of steel). The commenter indicated that it was not clear whether the listing description applied only to primary steel production or to both primary steel producers and to foundries using steel scrap in their electric furnace production.

In listing waste K061 (Emission control dust/sludge from the electric furnace production of steel), the Agency intended only to include wastes from primary steel production. This intent is reflected in the listing background document, which refers throughout to primary steel production. The Agency is uncertain whether foundry electric furnace emission control dusts and sludges are sufficiently similar in composition to warrant inclusion in the same listing, and so we are evaluating the potential hazardousness of foundry industry wastes in separate actions. (See 44 FR at 49404 (August 22, 1979), and 45 FR at 47836 (July 16, 1980).)

## References

- a. U.S. EPA, Reivews of the Enviromental Effects of Pollutants; III Chromium. ORNL/EIS-80; EPA-600/1-78-023; May 1980.
- b. Transistion Metal Chemistry, R.L. Carlin, ed. Marcel Dekker, New York. 1965; Volume 1.
- c. Bartlett, R.J. and J.M. Kimble. Behavior of Chromium in Soils: I Trivalent Forms. J. Environ. Qual. 5: 379-383: 1976.
- d. Griffin, R.A., A.K. Au, and R.R. Frost. Effects of pH on adsorption of chromium from landfill leachate by clay minerals. J. Environ. Sci. Health A12(8): 430-449:1977.
- e. U.S. EPA. Application of Sewage Sludge to Cropland; Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals. EPA 430/9-76-013. NTIS PB No. 264-015. November, 1976.
- f. Bartlett, R.J. and J.M. Kimble. Behavior of Chromium in Soils: II Hexavalent Forms. Ibid. 5:383-386. 1976.

## LISTING BACKGROUND DOCUMENT

## Steel Finishing

## Spent Pickle Liquor (C) (T)\*

I. Summary of Basis for Listing:

Spent pickle liquor is generated in the pickling of iron and steel to remove surface scale. The Administrator has determined that spent pickle liquor is a solid waste which may pose a present or potential hazard to human health and the environment when improperly transported, treated, stored, disposed of, or otherwise managed, and, therefore, should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. Spent pickle liquor is corrosive (has been shown to have pH less than 2), and contains significant concentrations of the toxic metals lead and chromium.
2. The toxic metals in spent pickle liquor are present in highly mobile form, since it is an acidic solution. Therefore, these hazardous constituents are readily available to migrate from the waste in harmful concentrations, causing harm to the environment.

\*In response to comments received by the Agency on the interim final list of hazardous waste (45 FR 33124, May 19, 1980), sludge from lime treatment of spent pickle liquor has been removed from the hazardous waste list (see Response to Comments at the back of this listing background document for more details).

3. Current waste management practices of untreated spent pickle liquor consist primarily of land disposal either in unlined landfills or unlined lagoons which may be inadequate to prevent the migration of lead and chromium to underground drinking water sources. Treatment of the spent pickle liquor by neutralization is also commonly practiced by the industry in which case, a lime treatment sludge is generated.
4. A very large quantity (approximately 1.4 billion gallons of spent pickle liquor) is generated annually. There is a great likelihood of large-scale contamination of the environment if these wastes are not managed properly.
5. Damage incidents have been reported that are attributable to the improper disposal of poorly treated spent pickle liquor.

## II. Industry Profile and Process Description

Pickling operations are very widespread across the United States. Spent pickle liquor is generated at 240 plants located in 34 states. Approximately 70% of these plants are situated in Pennsylvania, Ohio, Illinois, Indiana and Michigan. Pickling capacity within the iron and steel industry, according to the type of acid used, is shown in Table 1 below.(1)

The pickling operation involves the immersion of oxidized steel in a heated solution of concentrated acid or acids (the pickling agent) to remove surface oxidation or to impart specific surface characteristics. At integrated steel plants, acid pickle liquors are used in cold rolling mills and galvanizing mills. Depending on the type of steel being processed, or the type of surface quality desired, different types of acids may be used. For example, most carbon steels are pickled in sulfuric

or hydrochloric acids, while most stainless and alloy steels are pickled in a mixture of nitric and hydrofluoric acids.(1) After a certain concentration of metallic ions build up in the pickling bath, the solution is considered spent or exhausted and must be replaced.

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Table 1

<u>Pickling Agent</u>	<u>Number of Plants*</u>	<u>Annual Capacity, tons of steel/yr</u>
HCl	43	30,000,000
H <sub>2</sub> SO <sub>4</sub>	149	28,000,000
Mixed acid (e.g. HF-HNO <sub>3</sub> )	152	6,000,000

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### III. Waste Generation and Management

Approximately 1.4 billion gallons of spent pickle liquor are generated annually: 500 million gallons of spent sulfuric acid, 800 million gallons of spent hydrochloric acid, and 74 million gallons of a combination (mixed) of pickling acids.\*\* When treated with lime, spent pickle liquors form a spent pickle liquor lime treatment sludge.

The spent pickle liquor is a strongly acid solution (pH <1) containing very high concentrations of dissolved iron, and

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\*If the same plant uses two or three pickling agents, it is listed once for each agent used.

\*\*Estimates based on waste generation data contained in Reference 1.

significant amounts of many other metals, including chromium (26-4250 ppm).(1) Hexavalent chromium concentrations are rarely reported, but since steel is manufactured in an oxidizing environment, and at high temperatures, and since it is the purpose of the pickling operation to remove residual metal oxides from the steel surface, it is expected that the pickling liquor will, in fact, contain significant amounts of hexavalent chrome.

Approximately 40% of the mills utilizing the sulfuric acid pickling process discharge these and other pickling wastes after treatment to a receiving body of water. Another 45% of these mills have the spent pickle liquor hauled off-site by private contractors. Outside contract disposal services generally neutralize spent pickle liquors in unlined lagoons.(2) The remaining 15% of the sulfuric acid pickling mills either utilize deep well disposal, engage in acid recovery, or discharge the treated waste to Publicly Owned Treatment Works (POTWs) along with other pickling wastes which have undergone varying degrees of treatment. Disposal practices of combination acid pickling mills and hydrochloric acid pickling mills are known to be similar to those used by sulfuric acid pickling mills.(1)

#### IV. Hazardous Properties of the Waste

The pickling process requires highly acidic solutions; hence, spent pickle liquors are highly corrosive, with a

pH of less than 2 (see Table 2). Therefore, this waste meets the corrosivity characteristic (§261.22) and is thus defined as hazardous. In addition, Agency data indicate that significant levels of the toxic metals lead and chromium are found in the spent pickle liquor (see Table 2 below).

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Table 2  
Typical Concentrations of Lead and Chromium in  
Spent Pickle Liquors(mg/l)

<u>Parameter</u>	<u>H<sub>2</sub>SO<sub>4</sub>Bath</u>	<u>HCL Bath</u>	<u>Mixed Acid Bath</u>
pH	1.0-2.0	1.0-4.5	1.3-1.5
Cr	26-269	2-37	3300-4250
Pb	ND*-2	2-1550	1-4

\*ND=Nondetectable

Source: Reference 1

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Based on the higher concentration levels listed in Table 2 for chromium and lead (4250 and 1550, respectively), if only .12% of the chromium (if hexavalent) and .33% of the lead leach from the spent pickle liquor, this amount would exceed the permissible concentrations of chromium and lead in the EP extract.\* Since the spent pickle liquor is a highly acidic solution, these toxic metals are readily available to migrate into the environment, as they are more

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\*The concentrations of lead and chromium in these wastes can vary, depending upon the composition of the raw materials used to manufacture the steel and the particular type of steel pickled.

soluble in acidic environments.<sup>(6)</sup> In particular, since trivalent chromium has only slight solubility in acids and the hexavalent form is extremely soluble, the chromium in the acid leachate will be overwhelmingly hexavalent. Thus, disposal of this waste in landfills or lagoons, if improperly managed, is likely to lead to the migration of harmful constituents into the environment and pose a substantial hazard via a groundwater exposure pathway.

#### Possible Types of Improper Management and Available Pathways of Exposure

As shown above, disposal of spent pickling liquors creates the potential for leaching of the toxic metals (presumably hexavalent) chromium and lead to groundwater, a common source of drinking water. In addition, improper storage and/or disposal of spent pickling liquor poses potential hazards stemming from the high acidity of the wastes. In particular, if not segregated in a landfill, spent pickle liquors can extract and solubilize toxic contaminants (especially metals) from other wastes disposed in the landfill. In view of the low solubility of most trivalent chromium compounds, and the high solubility of most hexavalent forms (see Attachment I), the leachate is expected to contain predominately the hexavalent form. If not stored in special containers, pickle liquors can, over time, corrode the containers, resulting in leakage and potential acid burns to individuals who may come in contact with the waste.

Transportation of about 45% of the spent pickle

neutralization (see p.4, above) increases the likelihood of their causing harm to people and the environment. Improper containment of these wastes may result in their doing harm to individuals or to the environment during transportation to their designated destination. Moreover, mismanagement of these wastes during transportation may result in their not reaching their designated destination at all, thus making them available to do harm elsewhere.

Once released from the matrix of the waste, lead and (presumably hexavalent) chromium can migrate from the disposal site to ground and surface waters used as or constituting potential drinking water sources. Present practices associated with landfilling or impounding the waste may be inadequate to prevent such an occurrence. For instance, selection of disposal sites in areas with permeable soils can permit contaminant-bearing leachate from the waste to migrate to groundwater.

An overflow problem might also be encountered if the liquid portion of the waste has been allowed to reach too high a level in the lagoon. Thus, a heavy rainfall could cause flooding which might reach surface waters in the vicinity.

In addition to difficulties caused by improper site selection, unsecure landfills in which wastes may be disposed of are likely to have insufficient leachate control practices. Available information, in fact, indicates that liners are not presently used in the landfilling or lagooning of these wastes.<sup>(1)</sup> There may be no leachate collection and treatment system to diminish leachate percolation through the wastes and soil

underneath the site to groundwater and there may be no surface run-off diversion system to prevent contaminants from being carried from the disposal site to nearby surface waters.

An additional regulatory concern is the huge quantities of these wastes generated annually. Spent pickle liquor is generated in very large quantities. The large quantities of this waste and the contaminants it contains pose a serious danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time since large amounts of pollutants are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or used up due to the large quantities of pollutants available.

#### V. Hazards Associated with Lead and Chromium

The lead and chromium that may migrate from the wastes to the environment as a result of such improper disposal practices are metals that persist in the environment in some form and, therefore, may contaminate drinking water sources for long periods of time. Hexavalent chromium is toxic to man and lower forms of aquatic life. Lead is poisonous in all forms. It is one of the most hazardous of the toxic metals because it accumulates in many organisms, and its deleterious effects are numerous and severe. Lead may enter the human system through inhalation, ingestion or skin contact.

Improper management of these wastes may lead to ingestion of contaminated drinking water. Aquatic toxicity has been observed at sub-ppb levels. Additional information on the adverse health effects of chromium and lead can be found in Appendix A.

The hazards associated with lead and chromium have been recognized by other regulatory programs. Lead and chromium are listed as priority pollutants in accordance with §307(a) of the Clean Water Act of 1977. National Interim Primary Drinking Water Standards have been established for both parameters. Under §6 of the Occupational Safety and Health Act of 1970, a final standard for occupational exposure to lead and chromium has been established and promulgated in 19 CFR 1910.1000.(8,9) Also, a national ambient air quality standard for lead has been announced by EPA pursuant to the Clean Air Act. (8) In addition, final or proposed regulations of the States of California, Maine, Massachusetts, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define chromium and lead-containing compounds as hazardous wastes or components thereof.(10)

#### VI. Damage Incidents\*

These damage incidents are attributable to the improper disposal of spent pickle liquor. They are just a few examples of the damage which may result if these wastes are mismanaged.

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\*Draft Environmental Impact Statement for Subtitle C, Resource Conservation and Recovery Act of 1976, Appendices-Reference 7.

- ° In Washington County, Pennsylvania, leachate from a landfill has entered the groundwater and has contaminated a farmer's well and spring a half mile away. The landfill accepts sludges containing heavy metals and poorly neutralized pickle liquor from steel mills.
  
- ° In April, 1975. An employee in York County, Pennsylvania, siphoned wastes from a company's settling pond into a storm drain emptying into a fishing creek. The acidity of the drained wastes caused a fish kill in the creek. The waste and sludge in the ponds were spent pickle liquors which had allegedly been neutralized. The sludge is to be hauled to a landfill and the lagoons are to be lined.

## References

1. U.S. EPA. Draft development document for the proposed effluent limitations guidelines and standards for the iron and steel manufacturing point source category; sulfuric acid pickling subcategory, hydrochloric acid pickling subcategory. v.8. EPA No. 440/1-79-024a. November, 1979.
2. U.S. EPA. Office of Solid Waste. Assessment of industrial hazardous waste practices in the metal smelting and refining industry. v.3. EPA No. SW-145c3. NTIS PB No. 276 171. April, 1977.
3. Waste characterization data from the State of Illinois EPA, as selected from State files by U.S. EPA/OSW on 3/14/79 and 3/15/79.
4. Waste characterization data from the State of Pennsylvania Department of Environmental Resources, Division of Solid Waste Management, March 20, 1978, as selected from State files by U.S. EPA/OSW, on 1/4/79 and 1/5/79.
5. Not used in text.
6. Pourbaix, M. Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, London. 1966.
7. Appendix J--Hazardous waste incidents, Draft Environmental Impact Statement for Subtitle C, RCRA. January 1979, as synopsised from Office of Solid Waste, Hazardous Waste Management Division; Hazardous Waste Incidents, unpublished open file data. 1978.
8. U.S. Department of the Interior, Bureau of Mines. Mineral commodity summaries. 1979.
9. NIOSH. Registry of toxic effects of chemical substances. U.S. Department of Health, Education and Welfare, National Institute for Occupational Safety and Health. 1977.
10. U.S. EPA States Regulations Files. January, 1980.
11. Not used in text.

## Attachment I

### SOLUBILITY AND ENVIRONMENTAL MOBILITY CHARACTERISTICS OF CHROMIUM COMPOUNDS

The tripositive state is the most stable form of chromium. In this state chromium forms strong complexes (coordination compounds) with a great variety of ligands such as water, ammonia, urea, halides, sulfates, amines and organic acids.(a,b) Thousands of such compounds exist. This complex formation underlies the tanning reactions of chromium, and is responsible for the strong binding of trivalent chromium by soil elements, particularly clays.(c,d)

At pH values greater than about 6, trivalent chromium forms high molecular weight, insoluble, "polynuclear" complexes of  $\text{Cr}(\text{OH})_3$  which ultimately precipitate as  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . This process is favored by heat, increased chromium concentration, salinity and time.(a) These chromium hydroxy complexes, formed during alkaline precipitation treatment of Cr-bearing wastes, are very stable, and relatively unreactive, because the water molecules are very tightly bound. In this form, Cr is therefore resistant to oxidation. Three acid or base catalyzed reactions are responsible for the solubilization of chromium hydroxide:

<u>Reaction</u>	<u>Keq. (18)</u>	<u>Cr(III) Concentration Calculated from keq (mg/l)</u>		
		<u>pH5</u>	<u>pH6</u>	<u>pH7</u>
1. $\text{Cr(OH)}_3 + 2\text{H}^+ \rightleftharpoons \text{CrOH}^{++} + 2\text{H}_2\text{O}$	$10^8$	520	5.2	0.052
2. $\text{Cr(OH)}_3 \rightleftharpoons \text{Cr}^{+3} + 3\text{OH}^-$	$6.7 \times 10^{-31}$	35	0.035	i*
3. $\text{Cr(OH)}_3 \rightleftharpoons \text{H}^+ + \text{CrO}_2^- + \text{H}_2\text{O}$	$9 \times 10^{-17}$	i	i	i

\*i = <0.001 mg/l

It is apparent from these figures that, in theory, trivalent chromium could leach from sludges to some extent. Such solubilized chromium, however, is unlikely to contaminate aquifers. It is complexed with soil materials, and tenaciously held. (a,d) Little soluble chromium is found in soils. (a,e) If soluble trivalent chromium is added to soils it rapidly disappears from solution and is transformed into a form that is not extracted by ammonium acetate or complexing agents. (c,e) However, it is extractable by very strong acids, indicating the formation of insoluble hydroxides. (d,e) Thus: above pH5, chromium(III) is immobile because of precipitation; below pH4, chromium(III) is immobile because it is strongly absorbed by soil elements; between pH 4 and 5 the combination of absorption and precipitation should render trivalent chromium quite immobile. (c,d)

In contrast, hexavalent chromium compounds are quite soluble, and hexavalent chromium is not as strongly bound to

soils.(c,i) Hexavalent chromium remains as such in a soluble form in soil for a short time, and is eventually reduced by reducing agents if present.(e,f) As compared with the trivalent form, hexavalent chromium is less strongly adsorbed and more readily leached from soils(d) and thus, is expected to have mobility in soil materials.(d)

## References

- a. U.S. EPA, Reivews of the Enviromental Effects of Pollutants; III Chromium. ORNL/EIS-80; EPA-600/1-78-023; May 1980.
- b. Transistion Metal Chemistry, R.L. Carlin, ed. Marcel Dekker, New York. 1965; Volume 1.
- c. Bartlett, R.J. and J.M. Kimble. Behavior of Chromium in Soils: I Trivalent Forms. J. Environ. Qual. 5: 379-383: 1976.
- d. Griffin, R.A., A.K. Au, and R.R. Frost. Effects of pH on adsorption of chromium from landfill leachate by clay minerals. J. Environ. Sci. Health A12(8): 430-449:1977.
- e. U.S. EPA. Application of Sewage Sludge to Cropland; Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals. EPA 430/9-76-013. NTIS PB No. 264-015. November, 1976.
- f. Bartlett, R.J. and J.M. Kimble. Behavior of Chromium in Soils: II Hexavalent Forms. Ibid. 5:383-386. 1976.

Response to Comments Spent Pickle Liquor and Sludge  
from Lime Treatment of Spent Pickle Liquor in Steel  
Finishing Operations

Spent Pickle Liquor from Steel Finishing Operations (K062)

One commenter requested that this particular listing be deleted, in its entirety, from the hazardous waste regulations. In the comment, it is pointed out that spent pickle liquor is widely used to precipitate phosphorous from wastewater in publicly owned treatment plants (POTW's). The commenter also states that pickle liquor is used for sludge conditioning. These practices have been the subject of numerous demonstration grants, research reports, major technology transfer promotions, etc., and the commenter argues that if pickle liquor is designated as hazardous, then many POTW's may be considered unrealistically to be storers and treaters of hazardous waste. Finally, the commenter indicates that in several literature reviews, including several EPA reports, it is stated that inorganic coagulants, precipitants and sludge conditioners, such as pickle liquor, contribute to the removal and precipitation of various components from wastewaters that were originally present from other natural sources and are not in themselves a significant source of toxic heavy metals such as Cr and Pb.

The short answer to this comment is that POTW's using spent pickle liquor in treatment operations are deemed to have

a permit by rule, subject to the conditions specified in §122.26(c) (45 FR 33435). Thus, the commenter's principal concerns have already been dealt with.

Moreover, the comment is misplaced in that it fails to challenge the Agency's determination that spent pickle liquor is hazardous. The Agency continues to stand on its finding that this waste stream is indeed hazardous. We note in this regard, that the American Iron and Steel Institute, whose members are among the principal generators of this waste, does not challenge the listing.

It may be that the commenter is arguing that the reuse of spent pickle liquor should not be deemed hazardous waste management.

As discussed in the preamble to the Part 261 regulations promulgated on May 19, 1980 (45 FR 33091-33095), the Agency has concluded that it does have jurisdiction under Subtitle C of RCRA to regulate waste materials that are used, reused, recycled or reclaimed. Furthermore, we reasoned that such materials do not become less hazardous to human health or the environment because they are intended to be used, reused, recycled or reclaimed in lieu of being discarded. Although the materials after being recycled and reclaimed may not pose a hazard, the accumulation, storage and transport of a hazardous waste prior to use, reuse, recycle or reclamation will present the same hazard as they would prior to being discarded. In addition, the act of use, reuse, recycling or

rec'amation', in many cases, poses a hazard equivalent to that encountered if the waste were discarded. Thus, the Agency believes it has a strong environmental rationale for regulating hazardous wastes that are used, reused, recycled or reclaimed.

For the particular wastes at issue, the Agency found that this waste for most or all of its existence prior to being recycled is stored in tanks or drums. If not stored in special containers, pickle liquors can corrode the containers, resulting in leakage and potential acid burns to individuals who may come in contact with the waste. Consequently, the waste must be considered a hazardous waste in this environment.

Sludge from Lime Treatment of Spent Pickle Liquor from Steel Finishing Operations

A number of comments were received which objected to the listing of sludge from lime treatment of spent pickle liquor from steel finishing operations as a hazardous waste. The commenters argue that the Agency's rationale for listing this particular waste is objectionable both on procedural grounds and on technical grounds. With respect to the procedural arguments, the commenters point out that the Agency has failed to articulate the bases for its conclusion, effectively precluding meaningful comment. In addition, they argue that in analyzing the listing background document, the Agency has ignored its own standards and procedures for determining hazardousness; and thus, they claim that the Agency

has violated fundamental principles of administrative law, and that its decision to list sludge from lime treatment of spent pickle liquor is unlawful.

On the technical side, the commenters argue that the Agency has relied on inadequate or inappropriate data to reach its conclusions, and that to the extent that the conclusion is discussed, none of the assertions are adequately substantiated in the listing background document or references cited therein. For example, the commenter points out that the listing background document does not show the specific data or go through the calculations from which EPA derived the "average" chromium and lead concentrations in the sludge. The most important objection, however, relates to the use of a single leaching test, using the Illinois EPA extraction procedure, to make the statement that leaching of chromium and lead has been shown to occur. The commenters took special exception to the use of the Illinois EPA extraction procedure, a test which calls for the addition of an unlimited amount of acid to maintain a pH of 4.9 to 5.2, rather than the U.S. EPA extraction procedure which calls for maintenance of acid conditions, but allows only limited acid addition. To refute the leaching argument, one commenter submitted data on leachate tests carried out by a number of steel companies using the Agency's extraction procedure (see Table 1).

Table 1  
 Leachate Analysis Using EPA's Extraction  
 Procedure on Sludge from the Lime Treatment  
 of Spent Pickle Liquor

Sludge Sample	Cr(mg/l)	Pb(mg/l)
6	0.002	0.006
12	0.002	0.004
28	0.002	0.002
1	0.05	0.15
2	0.03	0.19

The commenter felt that these data indicate that the sludge from lime treatment of spent pickle liquor is not hazardous because all concentrations are well below EPA's promulgated limit for classification as a hazardous waste. Therefore, the commenters recommended the sludge from lime treatment of spent pickle liquor be deleted from the list of hazardous waste.

The Agency strongly disagrees with the commenter that the Agency has ignored its own standards and procedures for determining the hazardousness of the waste. This particular waste (K063) was assigned a "T" hazard code, indicating a toxic waste. The listing criteria for toxic wastes provide that a waste will be listed as hazardous where it contains any of a number of designated toxic constituents, unless after consideration of certain specified factors (261.11(a)(3)), the Agency concludes that the waste does not meet part [B] of the statutory definition of hazardous waste.

In waste K063, the Agency identified two toxic constituents (chromium and lead) in the waste. The Agency then evaluated the toxicity of this waste based on a number of the factors cited in §261.11(a)(3) (i.e., concentration of the constituent in the waste, potential of the constituents to migrate from the waste, the persistence of the toxic constituents, plausible types of improper management, etc.). Based on the available data, the Agency felt that sludge from lime treatment of spent pickle liquor may present a substantial hazard to human health or the environment, if improperly managed. With respect to the commenters objection to consideration of data derived from use of the Illinois EPA extraction procedure, the Agency strongly believes that any extraction testing, whether used by the States, industry or Federal government, may be considered by the Agency in evaluating the migratory potential of the toxic constituents in the waste. §261.11(a)(3)(iii) does not require the Agency to use the EP but rather to assess "...the potential of the constituent or any toxic degradation product of the constituent to migrate from the waste into the environment under the types of improper management considered in paragraph (a)(3)(vii) of this section." For this particular waste, the Illinois EPA extraction procedure may be most appropriate for determining the potential mobility of the heavy metals in the waste because of the potential for this waste to be mixed with other acid wastes or the potential for the spent pickle liquor to be poorly neutralized (see section VI of the background document).

However, in recognition of the commenter's data, the Agency has decided to delete this waste from the interim final hazardous waste list, and to rely on the provisions of §261.3 to bring these wastes within the hazardous waste management system. Since these lime treatment sludges are generated from the treatment of a listed hazardous waste (K062), they are considered to be hazardous wastes (§261.3(c)(2)) and will remain as hazardous unless and until they no longer meet any of the characteristics of hazardous waste and are delisted (§261.3(d)(2)). The Agency does not believe that sufficient information has been submitted to exclude totally the waste from the hazardous waste regulations, however the Agency would consider an industry-wide rulemaking petition to exclude these wastes from Subtitle C jurisdiction if the industry presents representative data showing the wastes are not hazardous. It should be noted that the lime treatment itself will require a hazardous waste management permit, since it constitutes treatment of a hazardous waste.

**Non-Ferrous Smelting and Refining Industry**

## PRIMARY COPPER SMELTING AND REFINING

Acid plant blowdown slurry/sludge resulting from the thickening of blowdown slurry (T)

Summary of Basis for Listing

Acid plant blowdown slurry/sludge, resulting from the thickening of the blowdown slurry, is a waste stream from the treatment of the acid plant blowdown slurry at facilities where primary copper is smelted in a reverberatory furnace. The Administrator has determined that these sludges are solid wastes which pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed and, therefore, should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- 1) Acid plant blowdown slurry contains high concentrations of the toxic heavy metals lead and cadmium.\*
- 2) A large quantity of these wastes is generated annually (approximately 286,000 MT (dry weight) was produced in 1977) and this quantity is expected to increase to 360,360 MT by 1983.
- 3) A solubility study has shown that lead and cadmium can be leached from these sludges by even a mild (distilled water) leaching media. Therefore, even under the mild conditions, the possibility of groundwater contami-

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\*For concentrations of other listed toxic heavy metals that do not warrant waste listing, see Attachment 1.

nation via leaching will exist if these waste materials are improperly disposed.

- 4) Current waste management practices consist of storage or disposal in unlined lagoons. These waste management practices may not be adequate to prevent a hazard to human health and the environment.

## Discussion

### A. Profile for the Industry

A 1977 review (1) indicated that there were 15 primary copper smelters in the United States operated by eight companies. A more recent source (2) identifies seventeen primary smelters operated by nine companies. Table 1 lists the seventeen plants and their production capacities. Almost all of the smelting capacity is concentrated in the southwestern United States, primarily Arizona and New Mexico. An average smelter can be assumed to have a capacity of 100,000 metric tons per year (1). Total national production of copper is increasing, based on a comparison of total capacities cited by References 1 and 2.

### B. Manufacturing Process

Processing of copper includes mining, concentrating of ores, smelting and refining. The smelting process involves two basic steps (3). First, the copper concentrate is melted in a reverberatory furnace to yield matte, which is essentially a mixture of copper and iron sulfides. The matte is then fed to converters in which air oxidation converts the copper sulfate to impure copper and the iron sulfide to an iron

oxide/silicate slag that can be separated from the copper. The product resulting from the reverberatory furnace converter smelting is blister copper. Depending on the intended final use, the blister copper is purified by fire refining and electrolytic refining. A flow diagram for the primary copper smelting process is shown in Figure 1.

The source of the listed waste stream is also indicated in Figure 1. (Note that the reverberatory furnace slag is not included in the listing since data submitted during the comment period indicated that the contaminants in the slag tend not to migrate out of the waste.) Lead and cadmium, the metals that constitute the basis for listing, are always in the waste since they are always present in the basic raw material, namely copper ore.

### C. Waste Generation and Management

As indicated in Figure 1, the listed waste addressed in this document arises from the acid plant which constitutes the principal controller for removal of sulfur dioxide from furnace and converter off-gases (3). The converter off-gases typically contain 5% or more of sulfur dioxide (3). According to the Calspan report (1), the acid plant for an average 100,000 metric ton/year smelter generates a blowdown slurry at a rate of about 2,270 cubic meters/day. After thickening, the bulk of the solid content of slurry is recycled to the

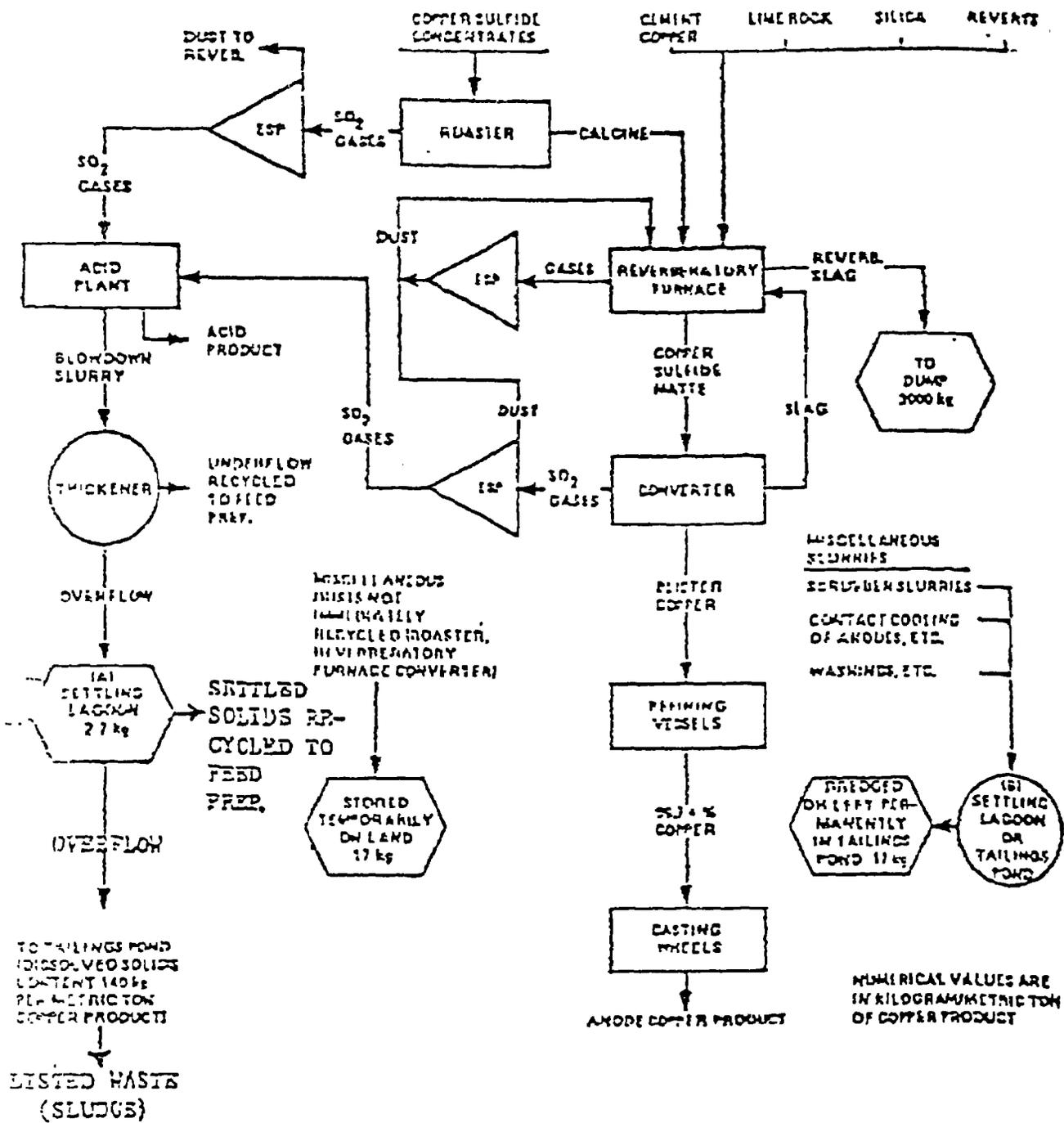


Figure 1 PRIMARY COPPER SMELTING AND FIRE REFINING

Source: Reference 1

reverberatory furnace.\* The overflow from the thickener - about 2,200 cubic meters per day, containing 0.77 metric tons of suspended solids and 40 metric tons of dissolved solids - is sent to a lagoon for settling. The suspended solid content is eventually recovered and recycled to the smelter.\* The 40 metric tons/day of dissolved solids remain in the aqueous lagoon effluent which is discharged to the main tailings pond.

Available documentation (1) indicates that this sludge is allowed to accumulate, along with the tailings waste, in the tailings pond. There is no evidence that this sludge/tailings mixture is dredged out for further treatment or disposal. Available documentation also indicates that these tailings ponds are unlined. These unlined tailings ponds are, therefore, the point of disposal for the 40 MT/day of material from the acid plant blowdown slurry that is not recycled. In comparison, 46 MT/day of thickener underflow solids and 0.8 MT/day of the overflow suspended

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\*At this time, applicable requirements of Parts 262 through 265 apply insofar as the accumulation, storage and transportation of hazardous wastes that are used, reused, recycled, or reclaimed. The Agency believes that this regulatory coverage is appropriate for the subject wastes. The slurry/sludge is hazardous insofar as they are being accumulated and stored in surface impoundments and insofar as they may be stored in piles prior to recycling. This waste may not pose a substantial hazard during the recycling and, even though listed as a hazardous waste, this aspect of their management is not now being regulated.

Table 1  
GEOGRAPHICAL DISTRIBUTION AND CAPACITIES OF  
PRIMARY COPPER SMELTERS

<u>Company</u>	<u>Location</u>	<u>Smelting Capacity (MT*/yr)</u>
Anaconda	Anaconda, MT	198,000
ASARCO	Hayden, AZ	180,000
	El Paso, TX	115,000
	Tacoma, WA	100,000
Cities Service	Copper Hill, TN	22,000
Copper Range	White Pine, MI	90,000
Hecla Mining	Casa Grande, AZ	31,000**
Inspiration	Miami, AZ	150,000
Kennecott	Garfield, Utah	280,000
	Hurley, NM	80,000
	Hayden, AZ	80,000
	Mc Gill, NV	50,000
Magma	San Manuel, AZ	200,000
Phelps Dodge	Morenci, AZ	177,000
	Hidalgo, NM	140,000
	Douglas, AZ	127,000
	Ajo, AZ	70,000

\* MT - metric tons

\*\* Smelting is done by a leach process, but the plant has an acid plant associated with the roaster.

solids are eventually recycled during treatment of the acid plant blowdown slurry.

Table 2 summarizes the total quantities of acid plant blowdown slurries (and miscellaneous other small volume slurries) that are generated. A total of 286,000 metric tons (dry weight) of waste sludge from primary copper smelters was generated in 1977. It is estimated (1) that this quantity will increase by about 26% to 360,360 metric tons by 1983. The total quantity of waste sludge disposed of (not recycled) by primary copper smelters in 1977 was 128,400 metric tons (dry weight).

D. Hazards Posed by the Waste

1. Concentrations of Lead and Cadmium in the Waste Stream

The listed waste has been analyzed (1) and found to contain toxic metals. The concentrations found are summarized in Table 3.

Sludges also have been subjected to leaching tests and have been shown (1) to leach lead and cadmium in significant concentrations. The leaching tests in the Calspan Study (1) was performed on one sample by agitating one part waste with two parts distilled water (initial pH 5.5) for 72 hours. The mixture was then filtered and analyzed. Table 4 presents the concentrations found in the leachate from the sludge sample. As shown by the test results in Table 4, cadmium appears in concentrations 17,000 times the EPA National Interim Primary Water Standard, and lead

TABLE 2  
ESTIMATED TOTAL WASTE SLUDGES FROM PRIMARY COPPER SMELTERS  
IN 1977\* (METRIC TONS - DRY WEIGHT)

<u>State</u>	<u>Total Blowdown Slurry</u>	<u>Total Disposed</u>
Tennessee	2,300	1,000
Michigan	17,500	7,900
Texas	14,800	6,700
New Mexico	24,800	11,200
Montana	28,500	13,000
Utah	34,300	15,000
Arizona	143,600	64,600
Nevada	6,100	2,700
Washington	<u>14,100</u>	<u>6,300</u>
Total	286,000	128,400

\*A number of copper smelters which were in existence in 1974 are no longer in operation, thus, the wastes produced by these smelters are not included in this table.

Source: Reference 1, Table 7d

TABLE 3  
CONCENTRATIONS OF HEAVY METALS IN WASTE  
SLUDGES FROM PRIMARY COPPER SMELTERS (PPM)

<u>Metal</u>	<u>Sludges</u>
Cadmium	520
Lead	8000

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Source: Reference 1

appears in concentrations 150 times the National Interim Primary Standard.

The distilled water leaching procedure used in the Calspan tests (1) thus indicates that lead and cadmium will leach from the waste even when subjected to mild environmental conditions. A more aggressive leaching agent may lead to more substantial release of the toxic metals. Disposal/storage in a surface impoundment or landfill with an acidic environment will certainly enhance the solubility of lead and other metals, since their solubility is pH dependent (i.e., solubility increases as the pH decreases (4)).

The information on the solubility of the compounds coupled with the fact that solubilization can occur more readily due to the fine particulate composition of the sludges suggests that the metals present in the listed waste may be released from the acid plant blowdown under improper storage/disposal conditions.

Once released from the matrix of the waste, the toxic metals can migrate from the disposal/storage site to ground and surface waters utilized as drinking water sources. Present practices associated with impounding the waste may be inadequate to prevent such an occurrence. For instance, selection of disposal sites in areas with permeable soils can permit contaminant-bearing leachate

Table 4  
CONCENTRATIONS OF HEAVY METALS IN FILTERED DISTILLED  
WATER LEACHATE, PPM

	<u>Sludges</u>
Cadmium	8.4
Lead	7.8

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Source: Reference 1

from the waste to migrate to groundwater. This is especially significant with respect to ponded wastes because a large quantity of liquid is available to percolate through the solids and soil beneath the fill.

In addition to difficulties caused by improper site selection, the lagoon/tailing ponds are likely to have insufficient leachate and surface run-off control practices. Therefore, there may be no leachate collection and treatment system to diminish leachate percolation through the wastes and soil underneath the site to groundwater. Further, there may be no surface run-off diversion system to prevent contaminants from being carried from the disposal site to nearby surface waters.

An overflow problem would thus be encountered if the liquid portion of the waste has been allowed to reach too high a level in the lagoon/tailings pond; a heavy rainfall could cause flooding which might reach surface waters in the vicinity.

Should lead and cadmium migrate from this waste, they would persist in the environment (in some form) virtually indefinitely and, therefore, may contaminate drinking water sources for long periods of time. Furthermore, cadmium is bioaccumulated at all trophic levels. Lead can be bioaccumulated and passed along

the food chain, but not biomagnified. The likelihood of human exposure is thus increased.

The large quantities of this waste stream generated (a total of approximately 286,000 MT (dry weight) in 1977) is an additional factor supporting the listing of this solid waste as hazardous. As previously indicated, the waste from primary copper smelting is generated in substantial quantities and contains significant concentrations (See Table 3) of cadmium and lead. Large amounts of these metals from the waste sludge are thus available for potential environmental release. The large quantities of these contaminants pose the danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time, since large amounts of pollutants are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or used up due to the large quantities of pollutants available. All of these considerations increase the possibility of exposure to harmful constituents and, in the Agency's view, support a T listing.

## 2. Hazards Associated with Lead and Cadmium

As presented below, The actual toxicity of these harmful constituents is well documented.

A 1977 review (6) summarizes much of the available data on the toxicity of lead and cadmium. Capsule descriptions of adverse health and environmental effects based on Reference are summarized below; more detail on the adverse effects of lead, and cadmium can be found in Appendix A.

Lead is poisonous in all forms. It is one of the most hazardous of the toxic metals because it accumulates in many organisms, and its deleterious effects are numerous and severe. Lead may enter the human system through inhalation, ingestion or skin contact. Lead is a cumulative poison in humans, leading to damage in kidneys, liver, gonads, the nervous system and blood vessels. Lead compounds also have been reported to cause oncogenic and teratogenic effects in animals. Toxicity to aquatic organisms occurs at ppb concentrations.

Cadmium shows both acute and chronic toxic effects in humans. The LD<sub>50</sub> (oral, rat) is 72 mg/kg of CdO. Cadmium and its compounds have been reported to produce oncogenic and teratogenic effects. Aquatic toxicity has been observed at sub-ppb levels.

The hazards associated with exposure to lead, and cadmium have been recognized by other regulatory programs. Lead and cadmium are listed as priority pollutants in accordance with §307(a) of the Clean Water Act of 1977. Under §6 of the Occupational Safety and Health Act of 1970, a final standard for occupational exposure to lead has been established (7,8). Also, a national ambient air quality standard for lead has

been announced by EPA pursuant to the Clean Air Act (8). In addition, final or proposed regulations of the States of California, Maine, Maryland, Massachusetts, Minnesota, Missouri, Mexico, Oklahoma and Oregon define cadmium or lead containing compounds as hazardous wastes or components thereof (9).

Attachment 1

These wastes contain measurable concentrations of certain other constituents listed in Appendix VIII of Part 261, including arsenic, chromium, mercury and selenium. The concentrations of these constituents in both the waste and distilled water leachate samples are, however, deemed insufficient to warrant listing the wastes on basis of these additional constituents, as demonstrated by the following tables:

CONCENTRATIONS OF HEAVY METALS IN WASTE SLUDGES  
FROM PRIMARY COPPER SMELTERS (PPM)

<u>Metals</u>	<u>Sludges</u>
Chromium	50
Mercury	0.8
Selenium	30

Source: Reference 1.

## REFERENCES

1. U.S. EPA, Office of Solid Waste. Assessment of hazardous waste practices in the metal smelting and refining industry, v.2. EPA No. SW-145c2. NTIS PB No. 276 170. April, 1977.
2. U.S. Department of the Interior, Bureau of Mines. Copper - mineral commodity profiles. September, 1979.
3. P. D. Dougall. Copper. In: M. Grayson and D. Eckoth, eds. Kirk-Othmer encyclopedia of chemical technology, 3rd. ed. v.6. John Wiley and Sons, New York. 1979.
4. Pourbaix, M. Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, London. 1966.
5. The Merck Index, 8th ed. Merck and Company, Inc, Rahway, NJ. 1968.
6. Cleland and Kingsbury. Multimedia environmental goals. v.2. EPA No. 600/7-77-136B. November, 1977.
7. U.S. Department of Interior, Bureau of Mines. Mineral commodity summaries. 1979.
8. NIOSH. Registry of toxic effects of chemical substances. U.S. Department of Health, Education and Welfare, National Institute for Occupational Safety and Health. 1977.
9. U.S. EPA States Regulations Files, Hazardous Waste State Programs, WH-565. U.S. EPA, 401 M St., S.W., Washington, D.C. 20460. Contact Sam Morekas (202) 755-9145. January, 1980.

## LISTING BACKGROUND DOCUMENT

## PRIMARY LEAD SMELTING

Surface impoundment solids contained in and dredged from surface impoundments at primary lead smelting facilities.(T)

Summary of Basis for Listing

The smelting of primary lead produces a number of wastewaters and slurries, including acid plant blowdown, slag granulation water, and plant washwater. These wastewaters and slurries are sent to treatment and storage impoundments to settle out the solids. The solids may be left in the lagoons, or they may be periodically dredged and disposed of elsewhere.

The Administrator has determined that the solids contained in and dredged from surface impoundments used to treat or store wastewaters and slurries from primary lead smelting may pose a present or potential hazard to human health or the environment when improperly managed and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

1. The waste contains significant concentrations of the toxic metals, lead and cadmium.

2. Significant concentrations of lead and cadmium have been shown to leach from samples of the waste which were subjected to an extraction procedure designed to predict the release of contaminants into the environment. If the wastes are not properly managed, leachate could migrate from the waste disposal site and contaminate underlying drinking water sources. Further, lead and cadmium do not degrade, so that contamination, and the opportunity for contaminant contact with living receptors, will be long-term.
  
3. Estimates indicate that large quantities of the waste are generated each year (more than 49,100 tons in 1978) and that the typical waste management practices may be inadequate to prevent substantial environmental harm caused by lead and cadmium migration.

#### Manufacturing Process and Sources of Hazardous Wastes (1)

The primary lead facilities that generate the hazardous wastes that concern EPA are four integrated lead smelter/refineries. These facilities are located in Missouri and Idaho. Production capacity ranges from 110,000 to 225,000 tons per year. Total primary lead production (from the four integrated smelter/refineries, two smelters and one refinery) was 611,650 tons in 1977. Forecasts indicate that domestic demand will increase to 1,030,000 - 2,340,000 tons in the year 2000.

All domestic smelters and refineries produce lead by pyrometallurgical smelting and refining processes. The major process steps are the same at all the smelters, with the exception that those that treat non-Missouri ore concentrates use auxiliary operations to recover valuable metals or remove undesirable impurities. The following is a step-by-step description of the manufacturing process as presented in Figure 1. This description includes the major process steps for all primary lead smelting and refining plants.

During the smelting process, concentrates produced by the beneficiation of various lead bearing ores are converted to an impure lead bullion suitable for refining. The ore concentrate is the major feedstock material. Other raw materials that may be added during the process include iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic, and particulates and sludges collected in pollution control devices. The ore concentrate and the pollution control dusts and sludges are the primary sources of lead and cadmium found in the settled solids from the surface impoundments.

The first of the processes in smelting is sintering, an operation which agglomerates the fine particles, converts metallic sulfides to oxides, drives off volatile metals, and eliminates most of the sulphur as sulphur dioxide. Off-gases from sintering may contain sulphur dioxides in concentrations that



are practical for recovery. Of particular concern, though, are the lead and cadmium entrained in those off-gases. Four plants have sinter machines designed to produce an off-gas containing enough sulphur dioxide to permit recovery of sulphur as sulphuric acid. The sulphur recovery operation generates a stream of weak acid called acid plant "blowdown". The acid plant blowdown stream contains lead and cadmium. Neutralization of the blowdown with lime usually generates a slurry destined for an on-site surface impoundment. This waste stream, resulting from the sulphur recovery operation, requires proper management.

In the second step in primary lead smelting and refining, sinter is charged to the blast furnace and smelted to crude lead bullion that can be further refined. During this reduction process, the components of the sinter are separated into four distinct layers, bullion, speiss, matte and slag. The two layers of concern are the bullion layer and the slag layer which result from the interaction of fluxes and metal impurities. The crude lead bullion is charged to drossing (the fourth step in this process.) The blast furnace slag may be disposed of or sent to a zinc fuming furnace (an interim step) for recovery of lead and zinc, rather than opting for direct disposal. The zinc fuming process, in turn, also generates a slag. Blast furnace slag and zinc fuming slag disposal practices are similar. The waste is either

sent directly to a slag pile or granulated in a water jet before being transported to the slag pile. The granulation process cools newly generated, hot slag with a water spray.

Slag granulation water is often transported to surface impoundments for settling.

The blast furnace bullion undergoes "drossing" (Step 4) to remove common metallic impurities. Dross separated from the lead bullion must be further treated in a reverberatory drossing furnace (Step 5) to recover metal values. Rough-drossed lead bullion, still containing copper, is decopperized (Step 6) before further refining. One of three usual processes is then used to remove metals that cause lead to harden. This process is called softening (Step 7). Softened lead bullion contains precious metals, gold, and silver, which are recovered for their economic value through the Parkes desilverizing process (Step 8). To remove the excess zinc added during desilverization, a dezincing process (Step 10) which removes the bismuth, which is in excess of the 0.15 percent specification for desilvered and dezincd lead bullion. Lead bullion from dezincing or debismuthing is combined with flux to remove remaining impurities before casting (Step 11) and, finally, the refined lead bullion is cast into ingots for sale (Step 12).

The listed hazardous wastes generated by primary lead

smelting plants are settled solids from surface impoundments. The impoundments are used to collect solids from miscellaneous slurries, such as acid plant blowdown, slag granulation water and plant washings. Plant washing is a housekeeping process; plant washdown normally contains a substantial amount of lead and other process material.

Data indicate that in 1978 four integrated smelter/refineries that process lead ore concentrates combined to produce more than 49,100 tons of impoundment solids considered hazardous. The data also indicate that the bulk of this waste is generated and managed at three plant locations.

The waste contains high concentrations of lead and cadmium. The presence of such high concentrations of toxic metals in a waste stream in and of itself raises regulatory concerns. Furthermore, distilled water extraction test data indicate that these dangerous constituents may leach from the waste in harmful concentrations unless the wastes are properly managed.

#### Waste Generation and Management (1)

As previously mentioned, the miscellaneous slurries generated by primary lead smelting plants are settled in

surface impoundments. Typically a minimal effort is expended for impoundment site selection. Site selection is based primarily on convenience. Site preparation usually consists of simply scooping out earth to form impoundments. EPA is unaware of any sealants or liners being employed beneath disposal areas. Leachate or groundwater monitoring is not adequately utilized, or not utilized at all.

Four facilities have surface impoundments. Currently, some of the impoundments are dredged of their accumulated solids on an "as needed" basis. Dredging is done with common equipment at frequencies from once per year to once every 3 years or longer. The dredged material is either dumped beside the impoundment or trucked to an on-site dump. Some of this material may be recycled to sintering if it contains enough metals.\*

#### Hazardous Properties of the Waste (3)

EPA has sampled process wastewater before and after treatment in an effort to quantify the amounts of lead and cadmium likely to be in the waste. The settled solids are assumed to contain the pollutants removed from the process wastewater. The data are summarized as follows:

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\*See "Response to Comments" at the end of this document for a discussion on the coverage of those materials recycled back to the process.

Plant A

Flow = 1,300,000 gpd (gallons per day)

Metal	Influent Concentration	Effluent Concentration	Difference	lbs/day in solids
Cd	0.89 ppm	0.044 ppm	0.846 ppm	9.172
Pb	17 ppm	0.925 ppm	16.075 ppm	174.3

Plant B

Flow = 280,000 gpd

Metal	Influent Concentration	Effluent Concentration	Difference	lbs/day in solids
Cd	15 ppm	0.43 ppm	14.57 ppm	34
Pb	50 ppm	0.39 ppm	49.61 ppm	115.85

Based on continuous year round plant operation, these data show that approximately 3300 lbs/yr of cadmium accumulate in an impoundment in Plant A and approximately 12,400 lbs/yr accumulate in Plant B. Lead in the impoundment solids from Plant A accumulates at a rate of almost 64,000 lbs/yr., and at a rate of almost 42,300 lbs/yr at Plant B. Should only one percent of each metal leach from the settled solids from Plant B, the result would be 124 lbs/yr of cadmium

and 423 lbs/yr of lead potentially available to the environment from that one plant.

The above evidence indicating that significant amounts of lead and cadmium are present in the settled solids is supported by actual waste analyses which reveal that the waste does in fact contain high concentrations of these toxic metals. The Calspan Corporation tested samples of the impoundment dredgings at two plants and found the following concentrations of lead and cadmium:(2)

Hazardous Constituents of Impoundment Dredgings (ppm)

	Cd	Pb
Plant I	700	115,000
Plant II	640	140,000

Calspan Corporation also subjected a sample of the waste believed to be representative of the lagoon dredgings to a water extraction to determine whether the toxic metals could leach from the waste. Approximately 50 grams of a sample was placed in a 200 milliliter jar and two parts by weight of water were added. The bottle was gently agitated on a rotary tumbler for 72 hours. The extract was then filtered through a 0.45 micron micropore filter and the filtrate was analyzed for toxic metals. This waste leached 11 ppm of

cadmium (1,100 times the amount permitted by the National Interim Primary Drinking Standard) and 4.5 ppm of lead (90 times the amount permitted by the National Interim Primary Drinking Standard). Therefore, cadmium and lead are likely to be leached from the waste in harmful concentrations even when they are placed in a monodisposal site subject to mild environmental conditions. If these wastes are placed in acidic environments such as disposal sites subject to acid rainfall or co-disposal with acids, the concentrations will probably be higher, since lead and cadmium compounds are generally more soluble in acid than in distilled water.

The hazard associated with leaching of hazardous constituents from the impoundments during the interim storage period is the migration of those constituents to ground and surface waters. The miscellaneous slurries are probably composed of particulates of various sizes, ranging from dust particles to fine slag from slag granulation water. The potential of the hazardous constituents being released from the matrix is influenced by the physical form of the waste. For instance, wastes composed of fine particles provide greater surface area on which a solubilizing medium can act and therefore the probability is increased that hazardous constituents will leach from the waste. Contaminant-bearing leachate can then migrate to ground and surface water.

Thus, improper disposal of surface impoundment solids may result in contamination of ground and surface waters by lead and cadmium. Aquatic species might be affected, and, where ground and surface waters are sources of drinking water, ingestion of the contaminants by humans could occur. For this reason, proper waste management is essential and of major concern to EPA.(2)

Present management practices appear to be inadequate to prevent contamination of ground and surface waters used as drinking water sources. Presently, if solids are allowed to settle in unlined and unsealed impoundments in areas with permeable soils, the solubilized lead and cadmium in the liquid phase could migrate from the site to an aquifer. Groundwater contamination might also occur if the dredged solids are dumped on permeable soils since no provision presently appears to be made to prevent percolation of rainfall through the waste or to collect resulting leachate. Surface waters may become contaminated if run-off from dumping sites and overflow from surface impoundments are not controlled by appropriate diversion systems.(2)

Compounding this problem, and an important consideration for the future, is the fact that should lead or cadmium escape from the disposal site, they will not degrade with

the passage of time, but will provide a potential source of longterm contamination.

Further, as indicated previously, the cadmium and particularly the lead found in the impoundments are generated in very substantial quantities. Large amounts of each of these metals are thus available for potential environmental release. The large quantities of these contaminants pose the danger of polluting large areas of ground and surface waters. Contamination could also occur for long periods of time, since large amounts of pollutants are available for environmental loading. The attenuation capacity of the environment surrounding the disposal facility could also be reduced or exhausted by such large quantities of pollutants. All of these considerations increase the possibility of exposure to harmful constituents in the wastes, and in the Agency's view, demand recognition.

#### Adverse Health Effects Associated with Lead and Cadmium

Lead and cadmium are toxic metals that threaten both human health and that of other organisms. The hazards of human exposure to lead include neurological damage, renal damage and adverse reproductive effects. In addition, lead is carcinogenic to laboratory animals, and relatively toxic

to freshwater organisms. It also bioaccumulates in many species. Additional information on lead can be found in Appendix A. Cadmium (see Appendix A for more information) also can cause toxic effects in many species. It is bioaccumulated at all trophic levels and has been shown to be mutagenic and teratogenic in laboratory animals.

Hazards associated with exposure to lead and cadmium have been recognized by other regulatory programs. For example, Congress designated lead and cadmium as priority pollutants under §307(a) of the Clean Water Act. The Occupational Health and Safety Administration has a final exposure standard for lead and a draft standard has been developed for cadmium under §6 of the Occupational Safety and Health Act of 1970. The states of Maine, Vermont, New Mexico, Missouri, Massachusetts, Minnesota, Oklahoma, Oregon, and California either regulate or are considering regulation of lead and cadmium as hazardous waste. The implications of these regulations or considerations thereof are obvious: unregulated lead and cadmium management is a real and recognized hazard.

1. U.S. EPA. IERL/ORD and Office of Solid Waste. Assessment of solid waste management problems and practices in nonferrous smelters. Prepared by PEDCO Environmental Inc., Contract No. 68-03-2577. November, 1979.
2. U.S. EPA. Office of Solid Waste. Assessment of hazardous waste practices in the metal smelting and refining industry. V's 1-4. NTIS PB Nos. 276 169, 276 170, 276 171, 276 172. April, 1977.
3. U.S. EPA. Office of Water Planning and Standards, Effluent Guidelines Division. Draft development document for effluent limitations guidelines and standards for the nonferrous metals manufacturing point source category. EPA No. 440/1-79/019c. September, 1979.

1. One commenter indicated that the listed waste (surface impoundment solids contained in and dredged from surface impoundments at primary lead smelting facilities) was recycled at his facility and, therefore, should not be listed as a hazardous waste.

The Agency has concluded that it does have jurisdiction under Subtitle C of RCRA to regulate wastewater treatment sludges and other waste materials that are used, reused, recycled or reclaimed. Furthermore, it has reasoned that such materials do not become less hazardous to human health or the environment because they are intended to be used, reused, recycled or reclaimed in lieu of being discarded. Although the materials recycled and reclaimed may not pose a hazard, the accumulation, storage and transport of a hazardous waste prior to use, reuse, recycle or reclamation will present the same hazard as they would prior to being discarded. In addition, the act of use, reuse, recycling or reclamation, in many cases, poses a hazard equivalent to that encountered if the waste were discarded. Thus, the Agency believes it has a strong environmental rationale for regulating hazardous wastes that are used, reused, recycled or reclaimed.

For the particular waste at issue, the Agency recognizes that it is a wastewater treatment sludge and for most or all of its existence prior to being recycled, it is deposited in a surface impoundment where the potential for leaching of the hazardous constituents is real and significant. Consequently, the waste must be considered a hazardous waste in this environment; to avoid listing it as a hazardous waste would be unjustified. Likewise, if the waste is piled and stored on the land, prior to recycling, the potential of leaching of its hazardous constituents into the environment would still prevail and avoiding its regulations would be unjustified.

The key question, therefore, is not whether or not it is a hazardous waste and should be listed as a hazardous waste, but whether or not or to what degree it should be regulated during recycling; that is, should the recycling process and facility be considered a hazardous waste management operation and facility required to obtain interim status and eventually a permit and required to meet the standards set forth in Parts 264 and 265 of the regulations. At this time, the Agency has deferred regulation of such facilities because it recognizes that the full set of Subtitle C management requirements may not be necessary. As and when it concludes that regulation of these facilities is necessary, it will terminate this

deferral and impose either the requirement of Parts 264 and 265 (as well as 122) or special tailored requirements under Part 266.

At this time, applicable requirement of Parts 262 through 265 and 122 will apply insofar as the accumulation, storage and transportation of hazardous wastes that are used, reused, recycled or reclaimed. The Agency believes this regulatory coverage and the above described deferral of regulated coverage is appropriate to the subject wastes. These sludges are hazardous insofar as they are being accumulated and stored in surface impoundments and insofar as they may be stored in piles prior to recycling. Therefore, these sludges should be listed as hazardous waste. These sludges may not pose a substantial hazard during their recycling and, even though listed as hazardous waste, this aspect of their management is not now being regulated.

LISTING BACKGROUND DOCUMENT  
PRIMARY ZINC SMELTING AND REFINING

Sludge from treatment of process wastewater and/or acid plant blowdown (T)

Electrolytic anode slimes/sludges (T)

Cadmium plant leach residue (iron oxide) (T)

Summary of Basis for Listing

The primary zinc industry is comprised of 7 plants that employ one of two major zinc manufacturing processes--electrolytic or pyrometallurgical processing. The five electrolytic and two pyrometallurgical plants recover zinc metal from ore concentrates. Cadmium and lead contaminants found in the raw materials are carried through numerous processes and are subsequently found in high concentrations in the wastewater treatment sludge generated by the treatment of process wastewater and/or acid plant blowdown, in the electrolytic anode slimes/sludges and in cadmium plant leach residue (iron oxide).

The Administrator has determined that these wastes are solid wastes which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- 1) The wastes contain significant concentrations of the toxic metals cadmium and lead.
- 2) Cadmium and lead have been shown to leach from samples of these wastes in significant concentrations

the neutralization and precipitation reactions in the WWTP, is continuously removed and hauled to an off-site landfill operated by a private contractor. At the plant that uses preleaching, the WWTP sludge also contains solids from acid plant blowdown, anode slimes (electrolytic cell cleanings), and miscellaneous slurries. The available information indicates that 9,400 tons of WWTP sludge is generated annually by this plant (3).

All zinc concentrates received at zinc plants are roasted to drive off sulfur and convert the zinc sulfide in the concentrate to an impure zinc oxide called calcine (3). The conversion to calcine in the roaster produces a roaster off-gas stream containing enough sulfur dioxide to permit sulfur recovery as sulfuric acid. All electrolytic plants treat the roaster offgas in sulfuric acid plants to produce a saleable sulfuric acid. The acid production results in a weak acid waste stream from the scrubbing columns that clean the off-gas. This waste is referred to as a bleed stream or acid plant blowdown. The acid plant blowdown is neutralized and thickened, and the solids are allowed to settle in ponds (3). Whether or not the solids are being stored for recycling, the solids do constitute a solid waste as defined by §261.2\*. Treatment of

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\*The Agency has concluded that it does have jurisdiction under Subtitle C of RCRA to regulate wastewater treatment sludges and other waste materials that are used, reused, recycled or reclaimed. Furthermore, it has reasoned that such materials do not become less hazardous to human health or the environment because they are intended to be used, reused, recycled or reclaimed in lieu of being discarded. Therefore, at this time, applicable requirements of Parts 262 through 265 and 122 will apply insofar as the accumulation, storage and transportation of hazardous wastes that are used, reused, recycled or reclaimed.

The acid plant blowdown generates an estimated 1,400 tons of sludge per year, (3) which has been designated as hazardous.

All electrolytic plants also generate a waste of anode slimes or sludges from cleaning of the electrolytic cells. Anode slimes/sludges consist of gangue material that is passed through earlier process steps but is not plated out, or electrolyzed, in the electrolysis step. It is estimated that anode slimes/sludges make up 2,600 tons of the annual solid waste produced (3). This waste is also designated as hazardous.\*

#### Pyrometallurgical Process

There are two pyrometallurgical zinc plants with a combined annual production rate of about 261,000 tons of zinc metal (3). These plants account for approximately 51 percent of the total production of zinc metal by the primary zinc industry, but 91 percent of the total solid waste produced by the industry. Although the two plants use the same basic processes (see Figure 2), they differ greatly in the quantities of solid waste generated and in the ultimate disposal or control of the waste (3).

Pyrometallurgical processing entails the following steps: sintering, retorting, refining and casting. Sintering develops the desired characteristics for pyrometallurgical smelting of the calcine by processing the calcine in a sinter machine where the

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\*All electrolytic plants also generate a leach residue from filtration of the leach slurry, which is not currently listed as hazardous and will not be further discussed in this background document.

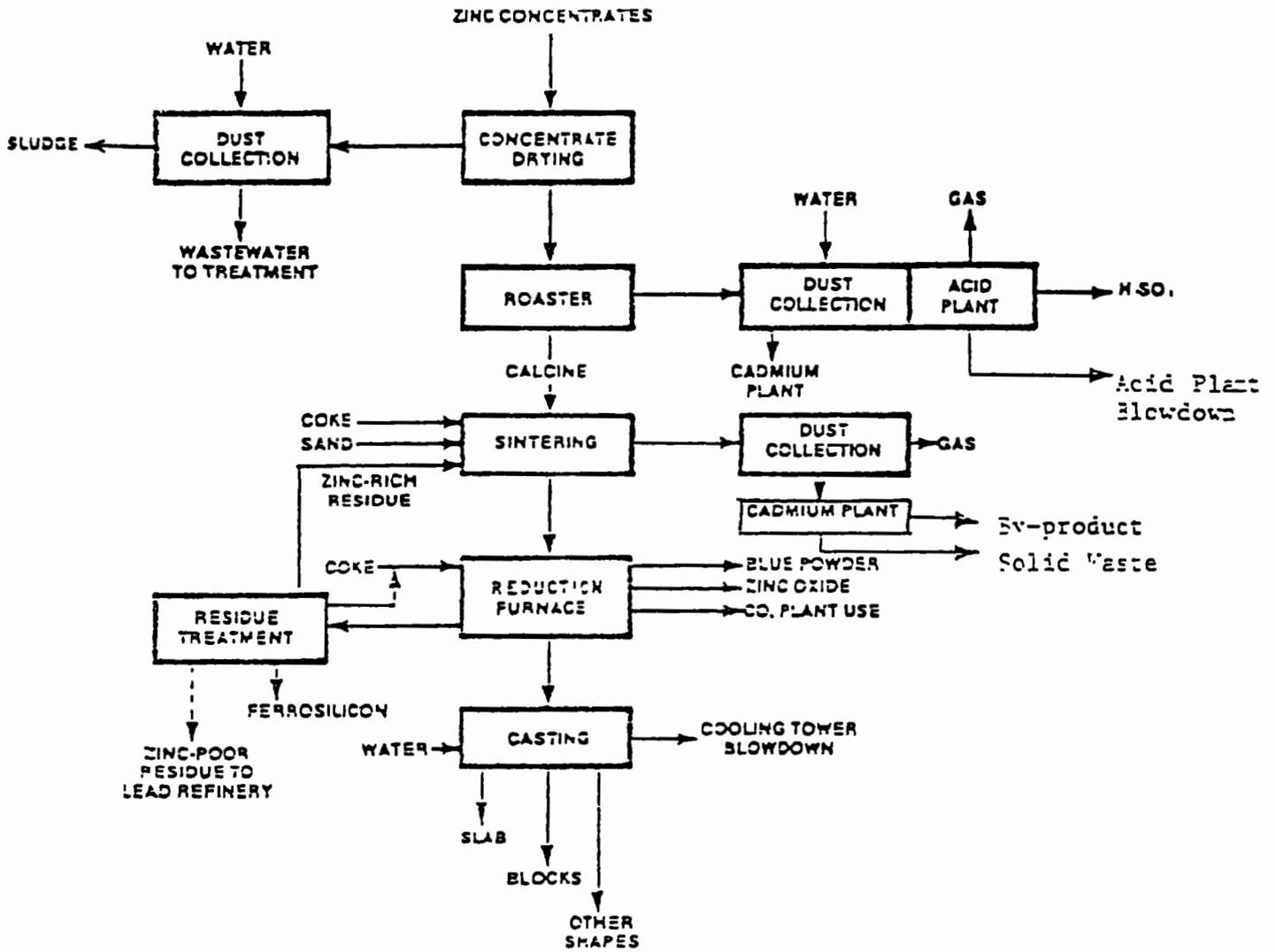


FIGURE 2. PYROMETALLURGICAL  
ZINC PRODUCTION PROCESS

calcine burns autothermally and is fused into hard, permeable sinter. Retorting consists of reducing the calcine in the sinter with carbon in a retort to produce zinc metal. Pre-heated feed of sinter and coal or coke is then fed into the top of the retort; the temperature reaches 1300°C-1400°C inside. Because of the zinc's low boiling point (906°C), it is volatilized as soon as it is formed. In this way the zinc is purified by separating it from the gangue material in the calcine. Zinc from the retort smelting may need further purification for some commercial uses. The zinc is purified by distillation in a graphic retort. Molten zinc from the graphic retort is either cast pure into bars or blocks or is alloyed with other metals and cast.

The sources of solid waste generated by the pyrometallurgical process which are hazardous are: (1) collection and treatment of acid plant blowdown, and (2) leaching of high-cadmium dusts in the cadmium plant (3).\*

Both pyrometallurgical plants treat roaster off-gas in their sulfuric acid plants to control sulfur dioxide emissions. The process is the same as the one described above for electrolytic plants. The acid plants produce a saleable sulfuric acid and a bleed stream (acid plant blowdown) that must be neutralized. One plant neutralizes the blowdown with lime, which leads to the generation of an estimated 10,000 tons per year of settled

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\*Two other wastes generated by this process (i.e., residue from the production of zinc oxide in Waelz Kins (one plant only) and furnace residue from the operation of retort and oxidizing furnaces) are not currently listed as hazardous and will not be further discussed in this background document.

sludge, half of which is recycled to the process. The sludge contains significant concentrations of cadmium and lead and is designated as hazardous.

The other pyrometallurgical plant uses the acid plant blowdown to cool and humidify the roaster off-gas in a humidifying scrubber. Acid plant blowdown from the scrubber is thickened and then cooled before being recycled to the scrubber. A bleed stream from the thickener bottoms is sent to the cadmium plant for cadmium recovery. This acid plant process generates no wastes.

Both of the pyrometallurgical plants operate cadmium plants to process dusts with high cadmium content that are collected from the sinter machine off-gas. Processing in the cadmium precipitation to produce a cadmium sponge. The leaching steps produce two residues. One contains relatively large quantities of lead, silver, and gold, and is sold as a by-product. The other residue constitutes a solid waste that contains cadmium and lead and is generated at a rate of 200 tons per year.<sup>(3)</sup> The latter residue has been classified as hazardous.

#### Waste Generation and Management (3)

At both the electrolytic and pyrometallurgical facilities off-gases from the roaster are treated in sulfuric acid plants to control sulfur dioxide emissions. This process generates acid plant blowdown which may be mixed with the process wastewater prior to treatment by lime precipitation.

The resulting sludge contains significant levels of lead and cadmium and is designated as hazardous.

Electrolytic refining generates a waste of anode slimes/sludges from cleaning the electrolytic cells. These slimes/sludges consist of gangue material that has passed through the earlier process steps but was not plated out in the electrolysis step. This waste also contains significant amounts of lead and cadmium and is designated as hazardous.

Pyrometallurgical plants process high cadmium dusts collected from the sinter baghouse to recover cadmium. Processing involves acid leaching which produces two residues. One contains significant amounts of lead, silver and gold; this residue is sold as a by-product. The other residue is a solid waste designated as hazardous because of its lead and cadmium content.

Current solid waste control practices are fairly uniform throughout the zinc industry. Of the total solid waste generated, about 90 percent is controlled through on-site stockpiling, 7 percent is removed by private and municipal organizations and individuals for various uses (such as winter road sand), and the remaining 3 percent is hauled and landfilled by private contractors.

#### Control Practices at Electrolytic Plants (3)

Electrolytic zinc plants produce solid waste consisting of anode "slimes/sludges", neutralized acid plant blowdown, surface impoundment dredgings, wastewater treatment sludge, and goethite residue.

Two of the electrolytic plants use wastewater treatment plants (WWTP) to treat plant wastewater and various process sludges. At both of these plants, the WWTP sludge is removed and hauled to off-site landfills. One of the two plants removes this sludge continuously as it is filtered (dewatered). There is no on-site storage or disposal at this plant. This particular sludge contains solids from anode sludge, neutralization of acid plant blowdown, impoundment dredgings, and sludge generated from the treatment of a preleach slurry. The other plant using a WWTP piles WWTP sludge on-site temporarily for drying prior to removal and transportation to an off-site landfill. This particular sludge contains solids from the neutralization of acid plant blowdown and solids precipitated from plant runoff and washdown. At this plant, anode sludge is not treated in the WWTP but is stockpiled on site. The WWTP sludge from these two plants amounts to about 31 percent of the solid waste generated at electrolytic plants. All of this sludge is hauled to off-site landfills, either immediately or after temporary on-site storage. Because the WWTP at each of these plants treats acid plant blowdown, the WWTP sludges generated containing cadmium and lead, are considered hazardous.

Two of the remaining three electrolytic plants stockpile dredgings from surface impoundments on-site. One of these plants generates two additional solid wastes that none of the other plants generate. These two wastes, goethite and a sulfur residue, are also stockpiled on-site.

Three of the four electrolytic zinc plants operating through 1978 used lined surface impoundments. Two of these plants use synthetic liners; the other uses a clay liner. The fourth plant has an unlined surface impoundment. Monitoring wells are used by at least one plant.(3)\*

It is assumed(3) that the fifth plant, one which has recently come on-line and will have a WWTP, will generate a sludge which will be removed to an off-site landfill. It is also assumed(3) that this plant will use a lined surface impoundment which treats the anode sludge, acid plant blowdown, impoundment dredgings, and plant wastewater in the WWTP. These assumptions, based on plant similarities indicated in the available literature(3), were necessary to estimate quantities of solid waste generation at this new facility. In order to avoid underestimation, the new plant is also assumed to generate a solid waste (such as goethite residue) that is stockpiled on-site.

#### Control Practices at Pyrometallurgical Plants

The two pyrometallurgical zinc plants produce acid plant blowdown, furnace (retort, oxide, and Waelz kiln) residue, scrap furnace brick, and a cadmium plant residue. One of these plants has a relatively small solid waste stockpile. The other pyrometallurgical plant has an extremely large stockpile of solid waste. This plant alone generates about 89 percent of the solid waste produced by all primary zinc

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\*The groundwater monitoring system at this one plant may not be sufficient to adequately monitor leaching from the surface impoundment.

plants(3). Solid waste stockpile sites are selected primarily for convenience. No site preparation is conducted other than clearing and grubbing.

Both plants have surface impoundments. The impoundment at one plant is lined with synthetic material; the impoundment at the other is not lined. At one plant, the impoundment collects acid plant blowdown and plant water. At the other plant, acid plant blowdown is not slurried to the impoundment, but is instead sent to the cadmium plant for further processing. Dredgings from both impoundments are controlled on-site. One plant recycles all dredgings to the process; the other recycles about half of the dredgings and stockpiles the remainder. One of the plants also stockpiles cadmium plant residues on-site.

These plants do not use surface water control by collection and diversion ditching to its fullest potential.(3) Neither do the plants currently use barriers to prevent seepage from solid waste stockpiles, or wells to monitor or collect any seepage or leachate(3).

#### Hazardous Properties of the Wastes

The Administrator has classified the process wastewater and/or acid plant blowdown treatment sludge, electrolytic anode slimes/sludges, and the cadmium plant leach residue (iron oxide) as hazardous because of the high levels of toxic cadmium and lead found in the wastes. In EPA's "Assessment of Hazardous Waste Practices in the Metal Smelting and Refining Industry," Calspan Corporation tested samples of the wastes

and performed extraction tests on the wastes using distilled water as the extraction medium (1). The results are as follows:

	<u>Waste Analysis (ppm)</u>		<u>Extract Analysis (ppm)</u>	
	<u>Cd</u>	<u>Pb</u>	<u>Cd</u>	<u>Pb</u>
Sludge from acid plant blowdown (Electrolytic Plant)	<10 <10 550	98 1750 18,100		2.1 1.0
Sludge from acid plant blowdown (Pyrometallurgical Plant)	2000 620	4350 4280	<0.01	1.3
Anode slimes/sludges	12 1400	170,000 89,000	1?	2.0
Cadmium Plant Residue	280	215,000	<0.01	9.0

Calculations of sludge contents from lime-and-settle wastewater treatment also indicate that significant amounts and concentrations of lead and cadmium are present in these wastes (2).

<u>Plant</u>	<u>Contaminants</u>	<u>Percent in Sludge</u>
#1	Cadmium	4.0%
	Lead	2.5%
#2	Cadmium	2.6%
	Lead	1.7%

Cadmium and lead are always expected to be in the sludges after treatment because 1) the treatment processes are designed to remove such elements from the wastewater to meet

effluent standards, and 2) cadmium and lead will not be lost (e.g., volatilized) in the treatment process.

Based on the data presented above, the waste is classified as hazardous because it contains significant concentrations of cadmium and lead which are toxic and because the extraction tests performed on these wastes indicate that the cadmium and lead may be in a soluble form and could be released to the environment in harmful concentrations. The fact that water extractions of the wastes have shown that the wastes could leach potentially hazardous concentrations of toxic metals indicates that under the mildest environmental conditions (e.g., neutral pH rainfall) at a mono-disposal site, the wastes may leach contaminants to the groundwater in concentrations which would be harmful to human health and the environment. Where conditions tend to be acidic, the release of these toxic metals over the lifetime of a landfill is expected to be even higher than indicated by the water extraction data, since cadmium and lead solubilities increase with a decrease in pH (4).<sup>1</sup>

On-site stockpiling is most likely not an environmentally acceptable means of disposing of a waste which contains

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<sup>1</sup>The Agency has determined to list wastes from primary zinc smelting and refining as a "T" hazardous waste, on the basis of lead and cadmium constituents, although these constituents are also measureable by the EP toxicity characteristic. The Agency believes that there are factors in addition to metal concentrations in leachate which justify the "T" listing. Some of these factors are the high concentrations of lead and cadmium in actual wastes streams, the non-degradability of these substances and indications of lack of proper management of the wastes in actual practice.

significant concentrations of toxic metals that have been shown to migrate from the waste. Surface water can become contaminated with contaminants from these wastes via runoff from rainfall. Similar hazards exist if these wastes are disposed of in improperly managed landfills or surface impoundments; leaching, run-off, or overflow may result in contamination of surface and groundwaters.

The cadmium and lead that may migrate from the waste to the environment as a result of improper disposal practices are toxic metals that persist in the environment and therefore may contaminate drinking water sources for extremely long periods of time. Cadmium is toxic to practically all systems and functions of the human and animal organism(5). Acute poisoning may result from the inhalation of cadmium dusts and fumes (usually cadmium oxide) and from ingestion of cadmium salts(6). Lead is poisonous in all forms; it is one of the most hazardous of the toxic metals because it accumulates in many organisms and the deleterious effects are numerous and severe. Lead may enter the human system through inhalation, ingestion or skin contact. Ingestion of contaminated drinking water is a possible means of exposure to humans as a result of improper management of these wastes. Additional information on the adverse health effects of cadmium and lead can be found in Appendix A.

The hazards associated with exposure to cadmium and lead have been recognized by other regulatory programs. Lead and

cadmium are listed as Priority Pollutants in accordance with §307(a) of the Clean Water Act of 1977. Under §6 of the Occupational Safety and Health Act of 1970, a final standard for occupational exposure to lead has been established (7). Also, a national ambient air quality standard for lead has been announced by EPA pursuant to the Clean Air Act (7).

In addition, final or proposed regulations of the State of California, Maine, Massachusetts, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define cadmium and lead-containing compounds as hazardous wastes or components thereof (8). EPA has proposed regulations that will limit the amount of cadmium in municipal sludge which can be landspread on crop land (9). The Occupational Safety and Health Administration (OSHA) has issued an advance notice of proposed rulemaking for cadmium air exposure based on a recommendation by the National Institute for Occupational Safety and Health (NIOSH) (10). EPA has prohibited ocean dumping of cadmium and cadmium compounds except as trace contaminants (11). EPA has also promulgated pretreatment standards for electroplaters which specifically limit discharges of cadmium to Public Owned Treatment Works (12).

### References

1. U.S. EPA, Office of Solid Waste. Assessment of hazardous waste practices in the metal smelting and refining industry. Vols. II and IV. EPA Nos. SW-145c2 and SW-145c4. NTIS PB Nos. 276 170 and 276 172. April, 1977.
2. U.S. EPA, Effluent Guidelines Division. Draft development document for effluent limitation guidelines and new source performance standards for the major nonferrous metals segment of the nonferrous manufacturing point source category. EPA No. 440/1-79/019. September, 1979.
3. U.S. EPA, Office of Solid Waste. Assessment of solid waste management problems and practices in nonferrous smelters. 1979.
4. Pourbaix, M. Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, London. 1966.
5. Waldbott, G.L. Health effects of environmental pollutants. C.V. Mosby Company, St. Louis. 1973.
6. Gleason, M.N., R.E. Gosselin, H.C. Hodge, B.P. Smith. Clinical toxicology of commercial products, 3rd ed. The Williams and Wilkins Co., Baltimore. 1969.
7. U.S. Department of Interior, Bureau of Mines. Mineral commodity summaries, 1980. December, 1979.
8. U.S. EPA State Regulations File, Hazardous Waste State Programs, WH-565. U.S. EPA, 401 M St., S.W., Washington, D.C. 20460. Contact Sam Morekas. (202) 755-9145.
9. 44 FR 53449.
10. 44 FR 5434.
11. 38 FR 28610.
12. 40 CFR, Part 413. Federal Register, Vol. 44, No. 175, Friday, September 7, 1979.

Response to Comments to Proposed Regulations (December 18, 1978)

Comments were received from three companies pertaining to the listing of wastes from the primary zinc industry.

The comments address the following general points:

1. Listed wastes are recycled and not discarded.
2. Listed wastes are being stored on-site but will eventually be recycled.

The Agency has concluded that it does have jurisdiction under Subtitle C of RCRA to regulate wastewater treatment sludges and other waste materials that are used, reused, recycled or reclaimed. Furthermore, it has reasoned that such materials do not become less hazardous to human health or the environment because they are intended to be used, reused, recycled or reclaimed in lieu of being discarded. Although the materials recycled and reclaimed may not pose a hazard, the accumulation, storage and transport of a hazardous waste prior to use, reuse, recycle or reclamation will present the same hazard as they would prior to being discarded. In addition, the act of use, reuse, recycling or reclamation, in many cases, poses a hazard equivalent to that encountered if the waste were discarded. Thus, the Agency believes it has a strong environmental rationale for regulating hazardous wastes that are used, reused, recycled or reclaimed.

For the particular wastes at issue, the Agency recognizes that these wastes for most or all of its existence prior to being recycled is deposited in a surface impoundment when the

potential for leaching of the hazardous constituents is real and significant. Consequently, the waste must be considered a hazardous waste in this environment; to avoid listing it as a hazardous waste would be unjustified. Likewise, if the waste is piled and stored on the land, prior to recycling, the potential of leaching of its hazardous constituents into the environment would still prevail and avoiding its regulation would be unjustified.

The key question, therefore, is not whether or not it is a hazardous waste and should be listed as a hazardous waste, but whether or not to what degree it should be regulated during recycling; that is should the recycling process and facility be considered a hazardous waste management operation and facility required to obtain interim status and eventually a permit and required to meet the standards set forth in Parts 264 and 265 of the regulations. At this time, the Agency has deferred regulation of such facilities because it recognizes that the full set of Subtitle C management requirements may not be necessary. As and when it concludes that regulation of these facilities is necessary, it will terminate this deferral and impose either the requirements of Parts 264 and 265 (as well as 122) or special tailored requirements under Part 266.

At this time, applicable requirements of Parts 262 through 265 and 122 will apply insofar as the accumulation, storage and transportation of hazardous wastes that are used,

reused, recycled or reclaimed. The Agency believes this regulatory coverage and the above described deferral of regulated coverage is appropriate to the subject wastes. These sludges are hazardous insofar as they are being accumulated and stored in surface impoundments and insofar as they may be stored in piles prior to recycling. Therefore, these sludges should be listed as hazardous waste. These sludges may not pose a substantial hazard during their recycling and, even though listed as hazardous waste, this aspect of their management is not now being regulated.

## LISTING BACKGROUND DOCUMENT

### SECONDARY LEAD SMELTING

Emission control dust/sludge from secondary lead smelting (T)

Waste leaching solution from acid leaching of emission control dust from secondary lead smelting (T)

#### I. Summary of Basis for Listing

The emission control dust/sludge from reverberatory furnace smelting of secondary lead products is generated when lead, cadmium, and chromium contaminants found in the source materials are entrained in the furnace fumes during the smelting process and subsequently collected by air pollution control equipment. Dry collection methods generate a dust as a solid residue; wet collection methods generate a sludge as a solid residue. The sludge is usually land disposed as a waste. The dust is usually recycled for further lead smelting; before recycling, however, the dust may be leached with acid for zinc recovery, and the resulting waste acid leaching solution containing cadmium, chromium and lead is land disposed. The Administrator has determined that these dusts/sludges and the waste acid leaching solutions from acid leaching of these dusts/sludges are solid wastes which may pose a substantial present or potential hazard to human health or the environment when improperly transported, treated, stored, disposed of or otherwise managed, and therefore should be subject to appropriate management requirements under Subtitle C of RCRA. This conclusion is based on the following considerations:

- 1) The emission control dusts/sludges contain significant

concentrations of the toxic metals lead, cadmium and hexavalent chromium.

- 2) Waste leaching solutions from acid leaching of the emission control dusts/sludges likewise contain significant concentrations of lead, cadmium, and hexavalent chromium, since the acid leaching medium solubilizes these heavy metals.
- 3) The hazardous constituents of these waste streams may migrate from the waste in harmful concentrations, since distilled water extraction procedures performed on samples of the emission control dust and sludge leached significant concentrations of cadmium and lead from the sludge and significant concentrations of lead, cadmium, and chromium from the dust.
- 4) The emission control sludge and the waste leaching solutions are typically disposed of in unlined lagoons, thus posing a realistic possibility of migration of lead, cadmium and hexavalent chromium to underground drinking water sources. Further, these elemental metals persist in the environment, thereby posing a real danger of long-term contamination.
- 5) Very large quantities of these emission control dust/sludges are generated annually (7,151,600 metric tons of sludge and 127,158,700 metric tons of dust in 1977) and are available for disposal as solid waste. There is thus greater likelihood of large scale contamination of the environment if these wastes are not managed properly.

#### I. Industry Profile and Manufacturing Process

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Eighty-two plants located in 27 states manufacture secondary lead products. The major production centers are located in the Great Lake States, in Texas and in Louisiana (1,5). Plant locations by state are shown in Table 1.

Plant capacities range from 25,000 to 40,000 metric tons of lead per year (1,5). The total quantity of lead produced by the secondary lead industry was 769,000 metric tons in 1978 and the estimate for 1979 is 760,000 metric tons (4).

Table 1 (1)

Distribution of Secondary Lead Smelters by State

<u>State</u>	<u>No. of Plants</u>
Alabama	2
California	8
Colorado	2
Delaware	1
Florida	3
Georgia	3
Illinois	7
Indiana	4
Kentucky	1
Louisiana	2
Maryland	1
Massachusetts	2
Michigan	4
Minnesota	1
Mississippi	1
Missouri	2
Nebraska	2
New Jersey	3
New York	4
North Carolina	2
Ohio	6
Pennsylvania	7
Texas	9
Tennessee	2
Virginia	1
Washington	1
Wisconsin	1

Four products are manufactured in the secondary lead industry: refined lead, lead oxide, antimonial lead and lead alloy. Individual plants may produce any or all of the products. As shown in Figure 1, the source materials will vary for each. Discarded batteries comprise the major source material. Other source materials are lead residues, lead slags and scrap iron.

## II. Generation and Management of Listed Waste Streams

### 1. Emission Control Dust/Sludge

Emission control dust/sludge is generated from the manufacture of refined lead, lead oxide, and lead alloy in reverberatory furnaces. In the production process, "soft lead" (low antimony lead) is smelted in a reverberatory furnace from lead residues, scrap lead, and, in the case of lead alloy, recycled secondary lead emission control dust is a source material. The soft lead is then further processed to either refined lead or lead oxide. In the scrubbing of reverberatory furnace emissions, cadmium, chromium and lead entrained in the fumes are collected by either wet scrubbing or by baghouse, resulting in a sludge or dust that may be discarded. The Agency attributes the presence of lead, cadmium and chromium in the waste stream to their presence in the source materials. (See p. 11 below confirming the presence of these toxic metals in the waste stream in significant concentrations.) The smelting processes takes place at high

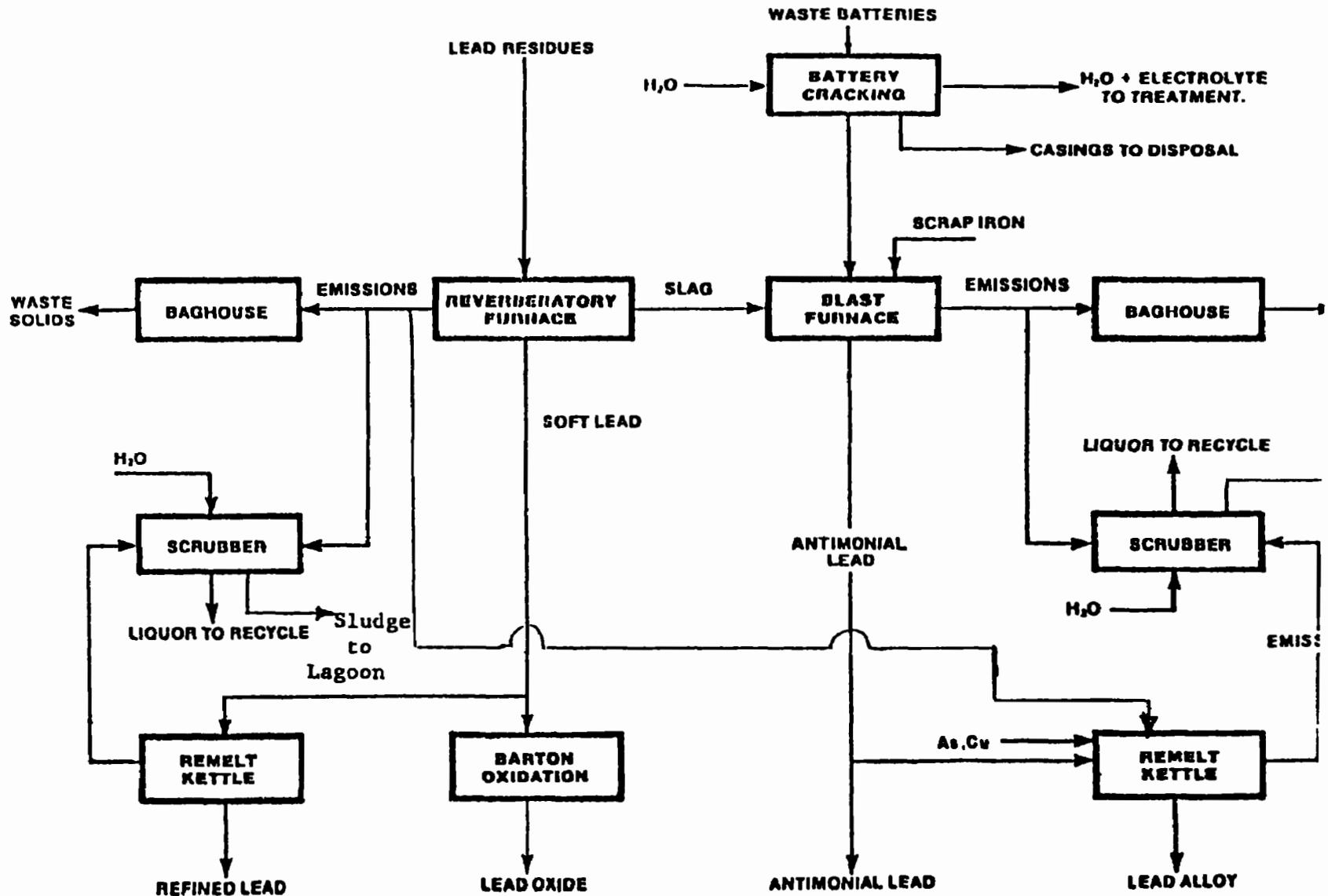


FIGURE 1. SECONDARY LEAD/ANTIMONY SMELTING PROCESS

temperatures, and in oxidizing atmospheres. Such conditions are known to cause oxidation of chromium to the hexavalent form.(12)

Three plants in the industry use wet scrubbing which generates a sludge. The sludge is typically disposed in unlined lagoons (1,5).

Dry collection methods (i.e., baghouses) are used by all other plants, generating a dust as a solid residue. This dust is available for disposal or for recycling.

## 2. Waste Leaching Solution

Emission control dusts are often recycled for use as input material for lead alloy ("white metal") production. The recycling process, however, generates a separate waste stream which is listed along with emission control dust/sludge. Before the dust is recycled to the remelt kettle for lead alloy production, it is leached with dilute sulfuric acid to remove zinc. The waste leaching solution contains chromium, cadmium, and lead leached from the emission control dust. Since trivalent chromium has only slight solubility in dilute sulfuric acid, and the hexavalent form is extremely soluble, the chromium in the acid leachate will be overwhelmingly hexavalent.

With regard to the management of the waste leaching solution, EPA is presently aware that a plant in New Jersey receives secondary lead emission dusts for recycling. The dusts are leached, and the waste acid solution is disposed of on-site in unlined lagoons (3). EPA presently lacks information

ON OTHER WASTE TREATING SOLUTION GENERATING LOCATIONS AND management practices.

The Agency wishes to make clear that it is not regulating those wastes which are recycled directly to the process as a hazardous waste. However, if the dusts are stored prior to recycling, they are defined as solid wastes and are subject to Subtitle C jurisdiction.\*

### 3. Secondary Lead Smelting Industry Waste Generation Levels and Trends

Generation of emission control dust/sludges from reverberatory furnaces is already very substantial, and is expected to increase in the future. Table 2 shows the historic sludge/dust generation from wet and dry scrubbing of reverberatory furnaces (5). Historic quantities are given for 1957 and 1977 as well as minimum and maximum generation projections predictions for 1980, 1984, and 1987. The total dust/sludge generation for 1977 (dry weight basis) was 127,158,700 metric tons. While not all of these materials are disposed (due to dust recycling), it is nevertheless clear that substantial quantities of wastes are generated annually.\*\*

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\*At this time, requirements of Parts 262 through 265 and 122 will apply to the accumulation, storage, and transportation of hazardous wastes that are used, reused, recycled or reclaimed. The Agency believes this regulatory coverage is appropriate to the subject waste. These dusts/sludges are defined as hazardous only if they are being accumulated and stored in piles prior to recycling. These dusts may not pose a substantial hazard during their recycling and, even though listed as a hazardous waste, this aspect of their management is not now being regulated.

\*\*The Agency presently lacks data to estimate the percentage of secondary lead smelting emission control dust which is recycled, although a major percentage of dusts generated may be recycled. In light of the large quantities of dust generated, the Agency believes large amounts of these dusts are managed as wastes, and not recycled.

TABLE 2. ATR POLLUTION CONTROL SLUDGE/DUST GENERATION -- REVERBERATORY FURNACES --  
SECONDARY LEAD INDUSTRY - (dry weight basis) (5)

State	SCC Code	Process	Total Sludge/Dust Generation (10 <sup>3</sup> metric tons/year)							
			Historic		Minimum Scenario			Maximum Scenario		
			1967	1977	1980	1984	1987	1980	1984	
		<u>Wet Controls</u>								
Illinois	3-04-004-02	Reverberatory furnace	4505.5	6490.8	6924.3	7718.4	8314.0	7755.7	8644.6	
Kansas	3-04-004-02	Reverberatory furnace	27.5	39.6	42.2	47.0	50.6	47.3	52.6	
Pennsylvania	3-04-004-02	Reverberatory furnace	431.2	621.2	662.7	738.7	795.7	742.2	827.3	
		Total sludge from wet controls	4964.2	7151.6	7629.2	8504.1	9160.3	8544.7	9524.5	
		<u>Dry Controls</u>								
Alabama	3-04-004-02	Reverberatory furnace	660.0	950.8	1014.3	1130.6	1217.8	1136.0	1266.3	
Arizona	3-04-004-02	Reverberatory furnace	8.3	11.9	12.7	14.2	15.3	14.2	15.9	
California	3-04-004-02	Reverberatory furnace	360.5	519.3	554.0	617.5	665.1	620.5	691.6	
Indiana	3-04-004-02	Reverberatory furnace	1849.6	2664.6	2842.6	3168.6	3413.1	3183.7	3548.8	
Louisiana	3-04-004-02	Reverberatory furnace	2481.2	3574.5	3813.2	4250.5	4578.5	4270.8	4760.5	
Minnesota	3-04-004-02	Reverberatory furnace	1327.3	1912.1	2039.8	2273.7	2449.2	2284.6	2546.5	
Mississippi	3-04-004-03	Reverberatory furnace	541.6	780.2	832.3	927.8	999.4	932.2	1039.1	
Missouri	3-04-004-03	Reverberatory furnace	2173.5	3131.2	3340.3	3723.4	4010.7	3741.1	4170.2	
Nebraska	3-04-004-02	Reverberatory furnace	7380.8	10633.1	11343.3	12644.2	13619.9	12704.5	14161.5	
N. Jersey	3-04-004-02	Reverberatory furnace	1856.2	2674.1	2852.7	3179.9	3425.3	3195.0	3561.5	
Ohio	3-04-004-02	Reverberatory furnace	550.0	792.3	845.2	942.1	1014.8	946.6	1055.2	
Tennessee	3-04-004-02	Reverberatory furnace	5403.0	778.4	830.4	925.6	997.0	930.0	1036.7	
Texas	3-04-004-02	Reverberatory furnace	62043.2	89382.4	95352.4	106288.1	114489.9	106794.7	119042.7	
Virginia	3-04-004-02	Reverberatory furnace	1187.9	1711.4	1825.7	2035.1	2192.1	2044.8	2279.3	
Washington	3-04-004-02	Reverberatory furnace	340.7	490.8	523.6	583.7	628.7	586.4	653.7	
		Total dust from dry controls	88163.8	120007.1	128022.5	142705.	53716.8	143385.1	159829.5	
		Total sludge/dust from wet/dry controls	93128.	127158.7	135651.7	151209.1	145319.8	151929.8	169354.	

These quantities can be expected to increase--particularly dust generation. First, New Source Performance Standards will limit particulate emissions from new reverberatory furnaces, resulting in increased collection of particulate wastes. Since baghouses are the most cost-effective means of meeting NSPS, it is expected that dry collection of emissions will continue to be used in the industry and lead to increased generation of emission control dusts (5).

Production of secondary lead is also increasing, again with the likely result of increasing emission control dust/sludge generation. Secondary lead production in fact increased by 200% between 1969 and 1979 (5). Projected dust/sludge generation levels (estimated on a minimum/maximum basis) are 145,319,800 - 274,475,700 metric tons (dry weight) by 1987 (Table 2).\*

### III. Hazardous Properties of the Wastes

#### 1. Concentrations of Lead, Cadmium and Chromium in the Waste Streams.

Agency data indicates that significant levels of the toxic metals lead, cadmium and chromium are found in the emission control dust/sludge. As indicated in Table 3, lead may comprise as much as 5 - 12% of the entire waste stream. Chromium and cadmium concentrations are also high (although nowhere near so elevated):

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\*The Agency does not presently have data showing quantities of waste leaching solution generated. Increased rate of emission control dust recycling may, however, lead to increased generation of waste leaching solution.

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Table 3(1)

	<u>Waste Analysis (ppm)</u>		
	<u>Cd</u>	<u>Pb</u>	<u>Cr</u>
Emission Control Sludge From Soft Lead Smelting	340	53,000	30
Emission Control Dust From Lead Alloy Smelting	900	120,000	150

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The Agency does not have metal concentration data for the waste leaching solution. Concentrations of these toxic metals in the waste leaching solution, however, can be expected to be significant since the acid leaching medium will solubilize cadmium, lead and hexavalent chromium fairly aggressively -- indeed, it is intended to perform this function. Some concrete idea of concentrations in the waste leaching solution can be gained from comparison of a distilled water extract of emission control dust presented in Table 4 below. Since lead and cadmium are more soluble in acid than in distilled water (7,8), and since most hexavalent chromium compounds are extremely soluble in all aqueous media (see Attachment I), the concentrations of these constituents in the dilute sulfuric acid leaching solution can be expected to be at least as great as, and more likely higher than concentrations in the distilled water extract.

2. Propensity of Lead, Cadmium, and Hexavalent Chromium to Migrate from the Wastes in Dangerous Concentrations and Possible Pathways of Exposure of Improperly Managed Wastes.

The presence of such high concentrations of toxic metals in a waste stream may pose a serious threat to human health and the environment should these toxic metals be released. Furthermore, distilled water extraction test data indicate that these toxic constituents may leach from the waste in harmful concentrations unless the wastes are properly managed. Thus, a distilled water extract from samples of the secondary lead emission control dust and emission control sludge presented in Table 3 indicates that lead, cadmium, and (in the case of the emission dust) chromium may solubilize from the waste in concentrations several orders of magnitude greater than Interim Primary Drinking Water Standards. See Table 4.

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Table 4(1)

	<u>Distilled Water Extract Analysis (ppm)</u>		
	<u>Cd</u>	<u>Pb</u>	<u>Cr (total)</u>
Emission Control Sludge From Soft Lead Smelting	5	2.5	.05
Emission Control Dust From Lead Alloy Smelting	230	24.0	12.0
Interim Primary Drinking Water Standard	.01	.05	.05

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While the Agency has not performed any analyses of the waste acid leaching solution, as noted above, the Agency believes lead, hexavalent chromium and cadmium concentrations in waste acid leaching solution will probably be higher than in the distilled water extract of the emission control dust. Furthermore, since the waste leaching solution may be disposed of in liquid form, i.e., with harmful constituents already solubilized and available for migration into the environment, there is a corresponding danger of exposure to harmful concentrations of these metals if the waste is improperly managed.

Thus, these wastes may leach harmful concentrations of lead, cadmium, and hexavalent chromium even under relatively mild environmental conditions. If these wastes are exposed to more acidic disposal environments, for example disposal environments subject to acid rainfall, these metals would most likely be solubilized to a considerable extent, since lead, and cadmium (including their oxides), as well as most chromium compounds, are more soluble in acid than in distilled water (6,7,8, and Attachment I). (See Table 1 indicating that a number of secondary lead plants are located in states known to experience acid rainfall including New Jersey, Ohio, Illinois, and Indiana.)

A further indication of the migratory potential of the waste constituents is the physical form of the waste itself. These waste dust/sludges are of a fine particulate composition, thereby exposing a large surface area to any percolating medium,

and increasing the probability for leaching of hazardous constituents from the waste to groundwater. Waste acid leaching solution, as noted above, is disposed of in liquid form with harmful constituents directly available for migration.

The Agency thus believes that emission control dust/sludge, and waste acid leaching solution may pose a threat of serious contamination to groundwater unless proper waste management is assured. These wastes do not appear to be properly managed at the present time. Thus, present industry practices of disposing of these wastes in unlined lagoons (see p. 7 above) may well not be environmentally sound. For example, location of disposal sites in areas with permeable soils could permit contaminant-bearing leachate from the waste to migrate to the groundwater in harmful concentrations. This is a particular concern for lagoon-disposed wastes because a large quantity of liquid is available to percolate through the solids and soil beneath the fill, increasing heavy metal solubilization and migration.

The Agency is also concerned that the lagooned wastes could contaminate surface waters if not managed to prevent flooding or total washout. While the Agency is not aware whether disposal lagoons presently have diking or other control mechanisms to prevent washout, it is certainly possible, given the number of sites, that in some cases, present flood-control measures are inadequate. Nor can proper flood management (or leachate control, for that matter) be assured without regulation.

Another pathway of concern is through airborne exposure to lead, chromium, or cadmium particulates escaping from emission control dust. These particulates could escape if waste dusts are piled in the open, or placed in uncontrolled landfills. For cadmium and hexavalent chromium compounds this pathway is known to be particularly dangerous (see Appendix A, Health Effects BD). Although the Agency is not aware whether waste dusts are managed in this manner, this type of improper management situation appears plausible in light of the large quantities of emission control dust generated annually.

Should lead, cadmium, or hexavalent chromium escape from the disposal site, they will persist in the environment and therefore may contaminate drinking water sources for extremely long periods of time. Cadmium is bioaccumulated at all trophic levels (9, 10). Lead can be bioaccumulated and passed along the food chain but not biomagnified.

3. The Large Quantities of Waste Dust/Sludge Generated Are A Further Factor Supporting a "T" Listing of These Wastes

The Agency has determined to list secondary lead emission control sludge/dust as a "T" hazardous waste, on the basis of lead, hexavalent chromium, and cadmium constituents, although these constituents are also measurable by the EP toxicity characteristic. Moreover, concentrations of these constituents in an EP extract from waste streams from individual sites might be less than 100 times interim primary drinking water

standards (although the Agency's own extraction data suggests that extract concentrations may exceed the 100 x benchmark for some generators). Nevertheless, the Agency believes that there are factors in addition to metal concentrations in leachate which justify the "T" listing. Some of these factors already have been identified, namely the high concentrations of cadmium and chromium (presumably largely in hexavalent form), and especially lead in actual waste streams, the non-degradability of these substances, and indications of lack of proper management of the wastes in actual practice.

The quantity of these wastes generated is an additional supporting factor.

As indicated above, secondary lead emission control dust/sludge is generated in very substantial quantities, and contains very high lead concentrations, as well as elevated concentrations of cadmium and (presumably hexavalent) chromium. (See p. 11 above.) Large amounts of each of these metals are thus available for potential environmental release. The large quantities of these contaminants pose the danger of polluting large areas of ground or surface waters. Contamination could also occur for long periods of time, since large amounts of pollutants are available for environmental loading. All of these considerations increase the possibility of exposure to the harmful constituents in the wastes, and in the Agency's view, support a "T" listing.

#### IV. Hazards Associated With Lead, Chromium and Cadmium

Lead is poisonous in all forms, and is one of the most hazardous of the toxic metals because it accumulates in many

organisms. Its deleterious effects are numerous and severe. Lead may enter the human system through inhalation, ingestion or skin contact.

The carcinogenicity of cadmium and its compounds, and of various hexavalent chromium compounds in humans is well documented;(13) EPA's CAG has determined that there is substantial evidence that cadmium and its compounds, as well as hexavalent chromium compounds are carcinogenic to man. The degree of absorption of hexavalent chromium compounds is higher than that for trivalent chromium, except when the latter is in some specific chemically-complexed form. Chronic toxicity problems associated with hexavalent chromium include damage to liver, kidney, skin, respiratory passages and lungs. Allergic dermatitis can result from exposure to both tri- and hexavalent chromium. Cadmium is toxic to practically all systems and functions of human and animal organisms(9). Acute poisoning may result from the inhalation of cadmium dusts and fumes (usually cadmium oxide) and from ingestion of cadmium salts (10). Additional information on the adverse health effects of cadmium, chromium, and lead can be found in Appendix A.

Lead, cadmium, and chromium historically have been regarded as toxic. Thus, EPA has established maximum concentration limits for lead, cadmium and chromium in effluent limitations guidelines adopted pursuant to Section 304 of the Clean Water Act, and under National Interim Primary Drinking Water

Standards adopted pursuant to the Safe Drinking Water Act. Lead also is regulated under the New Source Performance Standards of the Clean Air Act.

The Occupational Safety and Health Administration (OSHA) has set a work place standard for exposure to lead, cadmium and hexavalent chromium compounds.

In addition, several states that are currently operating hazardous waste management programs specifically regulate cadmium, chromium, and lead containing compounds as hazardous wastes or components thereof. These states include Maryland, Minnesota, New Mexico, Oklahoma and California (final regulations), and Maine, Massachusetts, Vermont, and Louisiana (proposed regulation).

## References

1. U.S. EPA. Office of Solid Waste. Assessment of hazardous waste practices in the metal smelting and refining industry, v.2 and v.4. EPA No. SW-145c2 and SW-145c4. NTIS PB Nos. 276 170 and 276 172. April, 1977.
2. U.S. EPA. Effluent Guidelines Division. Draft development document for effluent limitation guidelines and new source performance standards for the major nonferrous metals segment of the nonferrous manufacturing point source category. Washington, D.C. September, 1979.
3. U.S. EPA. Office of Solid Waste. Assessment of solid waste management problems and practices in nonferrous smelters. EPA No. 68-03-2577. November 1979.
4. U.S. Department of Interior, Bureau of Mines. Mineral commodity summaries. 1980. December, 1979.
5. U.S. EPA. Office of Solid Waste. Background document for comprehensive sludge study relevant to section 3002(9) of the Resource Conservation and Recovery Act of 1976 (P.L. 94-580). SCS Engineers. EPA Contract No. 68-01-3945. Volume 2, App. E. December, 1978.
6. CRC Handbook of Chemistry and Physics, 52nd ed. The Chemical Rubber Company, Cleveland, Ohio. 1971-72.
7. The Merck Index, 8th ed. Merck & Co., Inc., Rahway, NJ. 1968.
8. Pourbaix, M. Atlas of electrochemical equilibria in aqueous solutions. Pergamon Press, London. 1966.
9. Waldbott, G.L. Health effects of environmental pollutants. C.V. Mosby Company, St. Louis. 1973.
10. Gleason, M.N., R.E. Gosselin, H.C. Hodge, and B.P. Smith. Clinical toxicology of commercial products, 3rd ed. The Williams and Wilkins Co., Baltimore. 1969.
11. Not used in text.
12. Latimer, W.J. Mand, H. Hildebrand. Reference book of inorganic chemistry. MacMillan Company, N.Y., 1940.
13. Casaret, J. and J. Doull. Toxicology, the basic chemistry of poisons. MacMillan Company, New York. 1979.

Attachment I

SOLUBILITY AND ENVIRONMENTAL MOBILITY

CHARACTERISTICS OF CHROMIUM COMPOUNDS

The tripositive state is the most stable form of chromium. In this state chromium forms strong complexes (coordination compounds) with a great variety of ligands such as water, ammonia, urea, halides, sulfates, amines and organic acids.(a,b) Thousands of such compounds exist. This complex formation underlies the tanning reactions of chromium, and is responsible for the strong binding of trivalent chromium by soil elements, particularly clays.(c,d)

At pH values greater than about 6, trivalent chromium forms high molecular weight, insoluble, "polynuclear" complexes of  $\text{Cr}(\text{OH})_3$  which ultimately precipitate as  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . This process is favored by heat, increased chromium concentration, salinity and time.(a) These chromium hydroxy complexes, formed during alkaline precipitation treatment of Cr-bearing wastes, are very stable, and relatively unreactive, because the water molecules are very tightly bound. In this form, Cr is therefore resistant to oxidation. Three acid or base catalyzed reactions are responsible for the solubilization of chromium hydroxide:

<u>Reaction</u>	<u>Keq. (18)</u>	<u>Cr(III) Concentration Calculated from keq (mg/l)</u>		
		<u>pH5</u>	<u>pH6</u>	<u>pH7</u>
1. $\text{Cr(OH)}_3 + 2\text{H}^+ \rightleftharpoons \text{CrOH}^{2+} + 2\text{H}_2\text{O}$	$10^8$	520	5.2	0.05
2. $\text{Cr(OH)}_3 \rightleftharpoons \text{Cr}^{3+} + 3\text{OH}^-$	$6.7 \times 10^{-31}$	35	0.035	
3. $\text{Cr(OH)}_3 \rightleftharpoons \text{H}^+ + \text{CrO}_2^- + \text{H}_2\text{O}$	$9 \times 10^{-17}$	1	1	

\*1 = <0.001 mg/l

It is apparent from these figures that, in theory, trivalent chromium could leach from sludges to some extent. Such solubilized chromium, however, is unlikely to contaminate aquifers. It is complexed with soil materials, and tenaciously held. (a,d) Little soluble chromium is found in soils. (a,e) If soluble trivalent chromium is added to soils it rapidly disappears from solution and is transformed into a form that is not extracted by ammonium acetate or complexing agents. (c,e) However, it is extractable by very strong acids, indicating the formation of insoluble hydroxides. (d,e) Thus: above pH5, chromium(III) is immobile because of precipitation; below pH4, chromium(III) is immobile because it is strongly absorbed by soil elements; between pH 4 and 5 the combination of absorption and precipitation should render trivalent chromium quite immobile. (c,d)

In contrast, hexavalent chromium compounds are quite soluble, and hexavalent chromium is not as strongly bound to

is.(c,d) Hexavalent chromium remains as such in a soluble form in soil for a short time, and is eventually reduced by reducing agents if present.(e,f) As compared with the trivalent form, hexavalent chromium is less strongly adsorbed and more readily leached from soils(d) and thus, is expected to have mobility in soil materials.(d)

## References

- a. U.S. EPA, Reviews of the Environmental Effects of Pollutants; III Chromium. ORNL/EIS-80; EPA-600/1-78-023; May 1980.
- b. Transition Metal Chemistry, R.L. Carlin, ed. Marcel Dekker, New York. 1965; Volume 1.
- c. Bartlett, R.J. and J.M. Kimble. Behavior of Chromium in Soils: I Trivalent Forms. J. Environ. Qual. 5: 379-383: 1976.
- d. Griffin, R.A., A.K. Au, and R.R. Frost. Effects of pH on adsorption of chromium from landfill leachate by clay minerals. J. Environ. Sci. Health A12(8): 430-449:1977.
- e. U.S. EPA. Application of Sewage Sludge to Cropland; Appraisal of Potential Hazards of the Heavy Metals to Plants and Animals. EPA 430/9-76-013. NTIS PB No. 264-015. November, 1976.
- f. Bartlett, R.J. and J.M. Kimble. Behavior of Chromium in Soils: II Hexavalent Forms. Ibid. 5:383-386. 1976.

## **Petroleum Refining**

## References

1. U.S. EPA, Office of Solid Waste. Assessment of Hazardous Waste Practices in the Metal Smelting and Refining Industry. Calspan Corporation. EPA Contract Number 68-01-2604, April 1977, Volumes II and IV.
2. U.S. EPA, Effluent Guidelines Division, Draft Development Document for Effluent Limitation Guidelines and New Source Performance Standards for the Major Nonferrous Metals Segment of the Nonferrous Manufacturing Point Source Category. Washington, D.C. September, 1979.
3. U.S. EPA, Office of Solid Waste. Assessment of Solid Waste Management Problems and Practices in Nonferrous Smelters. PEDCo Environmental, Inc. EPA Contract Number 68-03-2577. November, 1979.
4. U.S. Department of Interior, Bureau of Mines. Mineral Commodity Summaries, 1980. December, 1979.
5. U.S. EPA, Office of Solid Waste. Background Document for Comprehensive Sludge Study Relevant to Section 8002 (9) of the Resource Conservation and Recovery Act of 1976 (P.L. 94-580). SCS Engineers. EPA Contract Number 68-01-3945. December, 1978. Volume 2, App. E.
6. Handbook of Chemistry and Physics, 52nd Edition. Cleveland, The Chemical Rubber Company, 1971-72.
7. The Merck Index. 8th Edition, 1968.
8. Pourbaix, Marcel. Atlas of Electrochemical Equilibria in Aqueous Solutions, London, Pergamon Press, 1966.
9. Waldbott, G.L. Health Effects of Environmental Pollutants. St. Louis, C.V. Mosby Company, 1973.
10. Gleason, M., R.E. Gosselin, H.C. Hodge, B.P. Smith. Clinical Toxicology of Commercial Products. Baltimore, The Williams and Wilkins Co., 1969. 3rd Edition.