

BACKGROUND DOCUMENT

RESOURCE CONSERVATION AND RECOVERY ACT

SUBTITLE C - IDENTIFICATION AND LISTING OF HAZARDOUS WASTE

§§261.31 and 261.32 - Listing of Hazardous Wastes (Phase IB)

July 7, 1980

U.S. ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF SOLID WASTE

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)(1) 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)(2) (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 aniline production, etc.)

- ° Commercial Chemical Products - these are a list of commercial chemicals or manufacturing chemical intermediates which if discarded either as the commercial chemical or manufacturing chemical intermediate itself; off-specification commercial chemicals 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 hazard waste is discussed in the background document entitled, "Hazardous Waste from Discarding of Commercial Chemical Products and the Containers and Spill Residues Thereof." This background document was made available to the public when Phase IA of Part 261 was promulgated (May 19, 1980).

HAZARDOUS WASTE FROM NON-SPECIFIC AND SPECIFIC SOURCES

Testing of pure substances is the traditional approach

used by regulatory agencies to control toxic/hazardous chemicals*. The purpose of RCRA, however, is to control waste materials; these are not normally pure substances (except as in the case noted above).

In order for a regulation to be effective, it should be structured so that it reflects the organization of the regulated community. Since waste process streams are often the units of the solid waste regulated by the Act, these same waste process streams can be used to provide a ready means of identification; such that, for our purposes, it is more useful (for identification purposes) to list "still bottoms from the XYZ process - ignitable". Likewise, there are certain waste classes, such as halogenated solvents which, if classified as wastes, would be unambiguously identified by such a designation.

In this document, the Agency is providing the technical support for the eighteen waste streams promulgated (interim final) under Phase IB of the hazardous waste regulations. (The technical support for the 85 waste streams promulgated interim final (45 FR 33123 - 33124) and 11 waste streams (45 FR 33137) proposed on May 19, 1980, under Phase IA has been available

*Pure substance listings work well for many agencies, since their responsibilities lie with some aspect of the pure substance. The Department of Transportation, for example, uses this approach. Benzene is listed by DOT as a flammable liquid. A transporter knows, after consulting the DOT listing, that benzene must be handled according to the DOT flammable liquid regulations.

for review and comment since May 19, 1980.) This document also includes the technical support for the seven new wastes proposed today. This listing (both interim final and proposed) includes two waste streams from non-specific sources and 23 wastes from specific sources. The background data used to support these listings comes 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.). The second source of data came from information collected from State Agencies (i.e., manifest data, etc.).

In addition, this document discusses the comments received on the proposed listings (43 FR 58957-58959 and 44 FR 49402-49404) which are promulgated interim final today, and the changes subsequently made.

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Generic

LISTING BACKGROUND DOCUMENT

PAINT APPLICATION PROCESSES USED IN THE MECHANICAL AND ELECTRICAL PRODUCTS INDUSTRY

- o Paint Residues/Sludges* Generated from Industrial Painting in the Mechanical and Electrical Products Industry (T)**
- o Wastewater Treatment Sludges from Industrial Painting in the Mechanical and Electrical Products Industry (T)

I. SUMMARY OF BASIS FOR LISTING

The waste streams listed above contain excess paint solids generated in industrial painting operations in the mechanical and electrical products industry. The waste streams contain elevated concentrations of toxic heavy metals and toxic organics.

Under Subtitle C of RCRA, the Administrator has determined that the above waste streams pose a threat to human health and the environment when improperly transported, treated, stored, disposed of or otherwise managed, and has designated these wastes as hazardous. This determination is based on the following considerations:

1. The paints used by the mechanical and electrical products industry contain numerous toxic constituents. These same constituents are also present in the excess paint wastes discharged in the subject waste streams. The specific toxic constituents of concern are: cadmium, chromium, lead, cyanides, toluene, and tetrachloroethylene. Chromium and tetrachloroethylene are believed to possess substantial evidence of carcinogenicity by the Agency's Carcinogen Assessment Group.

* The term 'sludge' in this context refers to oversprayed paint solids that are disposed of in a wet form.

**These wastes may often be ignitable, but at this time EPA does not have sufficient data to indicate that this is typically or frequently the case. Generator's are responsible for determining whether the waste meets the ignitability characteristic.

2. The toxic constituents of concern are all capable of migration, mobility, and persistence. Improper management of these wastes may result in the release of toxic constituents in these wastes to groundwater and to surface waters, resulting in substantial potential for hazard.

II. INDUSTRY PROFILE AND MANUFACTURING PROCESS

There are more than 88,700 individual manufacturing facilities associated with the Mechanical and Electrical Products Industries (M&EP).⁽¹⁾ These facilities are distributed throughout the 50 states with concentrations in the heavily industrialized areas. Painting is a common operation throughout the M&EP and is present at practically all facilities ⁽¹⁾. The paint consumption for a portion of the M&EP industry is given below and is expected to increase at an annual rate of 7.5 percent ⁽¹⁾.

<u>Industry</u>	<u>Million Gal/Yr</u>
Manufacture of Transportation Equipment	100
Manufacture of Metal Furniture	25
Manufacture of Prefinished Metal Stock	25
Manufacture of Machinery & Equipment	
(including electrical)	35
Manufacture of Appliances	20
Metal Decorating	50
Total	<u>255</u>

Paint Application Processes

Paints are uniform dispersions of inorganic and organic substances, which, after application to a surface, convert to a solid film. They may be used for protection, decoration or identification. All paints contain binders and most contain solvents, pigments and additives. Paint may be applied in several physical states: as a liquid (waterborne or organic solventborne); as a high solids coating (a form of liquid coating in which the liquid portion is small and the solids content is high); or as a powder (where there is virtually no solvent).

Paint application methods are by either spray or dip, or some variation thereof. Application may be manual or automatic. The major quantities of hazardous wastes are generated in the spray application method. Other techniques may generate minor quantities of wastes from clean-up between paint batches, spills, accidents and paint overspray.

There are six basic paint application techniques(1):

1. Spray Painting: Liquid spray painting is presently the most common application method and may be used with almost all varieties of paint to coat almost all types of materials. Varieties of spray application include air spray, airless spray, hydraulic spray, electrostatic spray and disc spray. All of these methods are amenable to automation and are currently in widespread use. In all cases, the

painting is accomplished by driving finely divided particles onto a workpiece. The particles may be atomized from a liquid by an atomizing spray gun, or they may be finely divided solid particles that are electrostatically charged at the spray gun and attracted to the piece to be coated.

Spray painting may also be done with powder. Powder overspray is generally collected and returned to the paint supply. However, powder overspray is occasionally intercepted by a water curtain, or collected dry and discarded.

2. Flow Coating: Flow coating is used to apply paint to materials of simple shape hung from conveyor lines. Paint flows under low pressure onto the parts. Excess paint is collected and recycled.
3. Dip Coating: Dip coating consists of submerging and withdrawing parts from a paint tank. Paint deposited on areas where it is not desired is removed with a water spray. The resultant waste may then be directed to the plant central wastewater treatment system, where it is removed along with sludge from other manufacturing processes.
4. Electrodeposition Coating: Electrodeposition (EDP) coating is used primarily to apply primer coats in the auto industry. It is a fast process which gives a fairly thick, highly uniform corrosion resistant coating.

The finishes produced by electrodeposition are not glossy. Therefore, spray painting is generally used for the final coat. In electrodeposition, parts which are immersed in a paint/water emulsion bath are coated by electrochemical action. The emulsion bath is continuously recirculated through an ultrafilter to remove impurities (which pass through the membrane into the permeate) and to provide rinse water. The permeate is split into a blowdown stream and a rinse water supply stream. The permeate stream is free of suspended solids, but if the blowdown portion is treated for dissolved heavy metals removal before discharge, some heavy metal sludge will result. After painting, the parts are rinsed first with ultrafiltration permeate and then usually with deionized water. The permeate rinse drainage is usually recirculated to the EDP paint bath, but the final, deionized rinse drainage is usually discharged. If treated before discharge, a very small quantity of paint solids may be removed from the water.

5. Fluidized Bed: The fluidized-bed process is used to apply powder coating. In this process, powder is first placed on a perforated plate forming the

bottom of a coating enclosure. Air is then blown into a chamber under the plate, fluidizing the powder. Coating occurs through heating or electrostatic means. In heating, the workpiece to be coated is heated to temperatures above the fusion point of the powder. The part is then dipped into the powder cloud and becomes coated as the powder melts on the surface of the workpiece. In an electrostatic fluidized bed, an electrode connected to a variable dc-voltage source is immersed in the powder. The charged particles of powder are attracted to the grounded workpiece and coat the surface.

6. Barrel Coating: Barrel coating is a means of coating batches of small objects, such as buttons or hardware. The parts are placed in a small cement mixer-like hopper and a carefully measured amount of paint is added. Fast drying paints, such as nitrocellulose lacquers are generally used. Drying is usually carried out in the hopper by continuing rotation with air injection.

III. WASTE GENERATION AND MANAGEMENT(1)

A. General Source of Waste

In the above paint application techniques, the rate of generation of hazardous waste will vary with the process used, while the actual contaminants generated will vary with the type of coating selected.

The paint use efficiency of several application methods is shown below(1):

<u>Method</u>	<u>Efficiency</u>
Conventional air spray	20 - 75%
Powder application	up to 99%
Dip coating	75 - 90%
Electrodeposition	90 - 96%
Electrostatic spray	up to 90%

Powder coatings are most efficient and have several advantages over liquid coatings. In powder coatings, virtually no solvents are used. Therefore, exhaust to the outside can be eliminated and instead, the air can be filtered and returned to the paint room. In addition, the dry powder overspray may be filtered out, eliminating the need for water or oil curtains. In some instances, the reclaimed powder coat can be reused after filtering and screening(1).

Liquid spray painting accounts for the majority of solid waste discharges within the industry. The source of waste solids in this process is overspray -- the paint which misses the object being painted. Overspray is intercepted by paper curtains or liners, by dry filter arrestors (which pass ventilating air), by water curtains, or by oil curtains. The paper curtains and dry filter arrestors are periodically disposed of as trash. Water and oil curtain interceptors rely on the circulation of water or oil continuously from,

and back to, sumps under the spray paint booths. The oversprayed paint solids are periodically removed from the sumps either manually or automatically. These wet solids are disposed of with the plant trash for removal by a contractor.

Some facilities discharge solids from paint booth sumps to an on-site wastewater treatment system. The paint solids, along with solids from other manufacturing processes, are then settled out as sludges in solids separating chambers such as clarifiers, settling tanks, and lagoons. All sludges are removed by contact haulers and disposed of in landfills.

B. Collection of Paint Residues

Paint booths are used to catch the excess paint overspray from a spray painting operation and to remove solvents in the air exhausted from the booth. The four common types of spray booths used in the spray painting industry and the associated wastes are described below.

1. Water-Wash Booths: Water-wash booths are common where there is a large volume of exhaust and overspray. Water reservoirs and water curtains are used to collect the excess paint and solvents. These booths are often tunnels, i.e., enclosed on the bottom, top, and sides. In a down-draft booth, where air flow is from top to bottom, the overspray is sucked down through a metal grating and into the water flowing below. Down-draft

booths are useful for large objects painted on more than one side, e.g. auto bodies. Through the addition of chemicals called paint killers, the overspray caught by the water may be made to float or sink in the reservoir located below the spray area.

When it is not feasible to float or sink the paint in the reservoir, the wastewater may be sent through an ultrafilter to remove the paint pigments in the liquid. This technique is most applicable to waterborne paints.

Electrostatic treatment also has been successfully used to treat the recirculating wastewater. The electrostatic treater incorporates an electrode to create an electric field through which the wastewater flows. The suspended paint particles are repelled by grounded piping or tanks, thus reducing buildup. Collected paint is disposed of or, in rare cases, may be reused.

2. Oil Wash Booths: In this type of booth, a special oil is used in place of chemically treated water. The oil facilitates recovery of the paint overspray and solvents that can be subsequently collected for disposal and/or reclaimed.

3. Powder Coating Booths: A typical powder coating booth has a wall with a steep, sloping bottom to collect the bulk of the powder overspray. The exhaust air from the booth is often sent to a centrifugal separator which separates the overspray from the air. Powder is discharged through the bottom of the chamber, and the cleaned air from the first stage separator is then sent to a bag filter to remove smaller suspended particles. Some plants then use an absolute filter and return the clean air to the plant. Recovered powder generally is blended with new powder and reused.
4. Dry Booths: In manual spray operations, the dry booth is usually enclosed on all but one side. Air is exhausted through the back after passing through disposable filters or around a series of staggered plates intended to catch most of the paint overspray. Exhaust rates are high enough to draw overspray paint away from the operator. The filters or paint scrapings are usually disposed of with plant trash.

Table 1 provides disposal data for paint residues/sludges from paint booths for 10 typical industrial plants. These were the only plant files, out of 56 examined, which contained sludge data. Listed are sludge volumes (or weight), disposal frequencies, the painting process and the number of paint

booths (or other source) for each plant(1). The frequency of disposal listed does not indicate the frequency of paint booth sludge skimming (which is often daily) but rather the disposal of accumulated sludge.

TABLE 1

QUANTITIES OF PAINT RESIDUES/SLUDGES GENERATED AT 10 PLANTS

EPA Plant Identification Number	Painting Process	Waste Volume (Or Weight)	Disposal Frequency	Waste Source
1002	Electrostatic Spray (water curtain booths)	3,680 yd ³	Annually	6 Booths
1007	Airless Spray Autodeposition	2.97 yd ³ 600 yd ³	Annually Annually	2 Booths 2 Production lines
1014	Electrostatic Spray (water curtain booths)	49 yd ³	Annually	2 Booths
1022	Spray Painting (water curtain booths)	25 yd ³	Biweekly	9 Booths
1024	Electroless Spray Dip Coating	1.38 yd ³ 0.27 yd ³	Monthly Monthly	4 Booths 2 Tanks
1025	Electrostatic Disc Powder Spray	20 lbs*	Weekly	--
1028	Electroless Spray (water curtain booths)	1,000 lbs	Weekly	--
1030	Electrostatic Spray (water curtain booths)	792.24 yd ³	Annually	7 Booths
1033	Electrostatic Spray (oil curtain booths)	1 yd ³	Monthly	6 Booths
1034	Electrostatic Spray (water curtain booths)	24.75 yd ³	Annually	1 Booth

(Approximately 5,830 yd³; average of 1,416,000 lb per plant)

*Weight includes disposable filter plus adhering paint overspray.

IV. HAZARDS POSED BY THE WASTE

1. Paint Residues/Sludges

These wastes are believed to frequently contain significant concentrations of the toxic metals cadmium, chromium, and lead, and the organic compounds toluene and tetrachloroethylene, and cyanides. The source of these toxicants is the paint itself. The primary source of data supporting this conclusion is data compiled from state hazardous waste manifests.⁽⁵⁾ This data shows these substances present in paint residues*, generally in very high concentrations (in some cases over 1% of the total waste, as in manifest numbers 3, 4, 5, 6, 7, 9, 10, 12, 17, and 19). Furthermore, in many cases, accompanying leachate extraction data shows that the toxic constituents are present in the waste in a highly mobile form, in some cases several orders of magnitude greater than the applicable National Interim Primary Drinking Water Standard. See manifests numbers 9, 10, 16, 17 and 19. It should also be noted that the generators of these wastes themselves consider their wastes to present "high ingestion toxicity", "high dermal toxicity", as in manifests numbers 11, 12, 14, 15, 16, 17, 20, 21, 22, 23, 24 and 25.

These data are presented below:

*Termed "sludges" in many of the manifests, although it is clear from the context that the wastes in question are paint residues, not wastewater treatment sludges.

1. State: Illinois

Source: Special Waste Disposal Applications

SIC: 3573

Waste Name: Solvent based paint sludge from the manufacture of electric computer equipment

Quantity: 1500 gallons (semi-solid)

Percent Analysis: 39% water

<u>Chemical Analysis:</u>	<u>Total concentration (ppm)</u>	<u>Leachate concentration (ppm)</u>
Cd	2.0	0.2
Cr	150	2.0

2. State: Iowa

Source: Reports of Special Waste, Iowa Department of Environmental Quality

Waste Name: Wall water spray booth paint sludge

Quantity: 365,200 lbs/year (sludge)

Chemical Analysis:

<u>Metal</u>	<u>Leachate Concentration (mg/l) (Deionized water)</u>	<u>Leachate Concentration (mg/l) (pH = 5.5)</u>
Pb	5.805	5.33

3. State: Kansas

Source: Industrial Waste Disposal Requests, Kansas Department of Health and Environment

Waste Name: Paint Sludge from overspray in spray booth in the manufacture of office furniture.

Quantity: 15-20 drums/mo.

<u>Quantitative Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>
	Cd	10,400
	Cr	2,900

4. State: Kansas

Source: Industrial Waste Disposal Requests, Kansas
Department of Health and Environment

Waste Name: Paint solids from water wash booths

Quantity: 400 bbls./year

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>
	Cr	750
	Pb	3,490

5. State: Kansas

Source: Industrial Waste Disposal Requests, Kansas
Department of Health and Environment

Waste Name: Paint booth waste

Quantity: 5 bbls/week (slurry)

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>
	Pb	216,000
	Cr	49,000

6. State: Kansas

Source: Department of Health and Environment, Industrial
Waste Disposal Requests.

Waste Name: Paint booth and machinery clean-up sludge

Quantity: 3000 gallons/month (slurry)

<u>Chemical Analysis:</u>	<u>Toxic Constituent Metal</u>	<u>Total Concentration (ppm)</u>
<u>Sample #1</u>		
	Pb	352
<u>Sample #2</u>		
Toluene		420,000
<u>Sample #3</u>		
Toluene		420,000

7. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3631

Waste Name: Paint Sludge from microwave oven manufacturing

Quantity: 40,000 gallons/year (solid)

Percent Analysis: 85% paint pigments

Flashpoint: 100°F

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>	<u>Leachate Concentration (pm)</u>
	Cr ⁺⁶	2,670	0.1
	Pb	130,000	0.1

8. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 2591

Waste Name: Paint Sludge from the manufacture of porch shades
and venetian blinds

Quantity: 1100 gallons/year (semi-solid)

Percent Analysis: 83% water
17% naptha
20% paint pigments

Flashpoint: 80°F

Other properties: High ingestion toxicity

9. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3519

Waste Name: Paint Sludge from spray curtain

Quantity: 25,000 gallons/bi-weekly (semi-solid)

Percent Analysis: 36% solids
10% water
54% volatile solids

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>	<u>Leachate Concentration (ppm)</u>
	Cr	2,500	15.0
	Pb	16,500	5.0

10. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3523

Waste Name: Paint Sludge from tractor cab manufacturing

Quantity: 17,600 gallons/year (solid)

Percent Analysis: 72.5% paint pigments
27.5% water

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>	<u>Leachate Concentration (ppm)</u>
	CN	150.0	--
	Cr+6	1500.0	1.3
	Pb	9200.0	5.4

Other properties: High ingestion toxicity

11. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3523

Waste Name: Paint sludge from farm machinery manufacturing

Quantity: 2000 gallons/year (semi-solid)

Percent Analysis: 85% pigments and filler
15% organic solvent

Flashpoint: 69°F

Other properties: High ingestion toxicity

12. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3531

Waste Name: Waste paint from spray booth from tractor manufacturing

Quantity: 24,000 gallons/year (semi-solid)

Percent Analysis: 66.5% water
30% paint pigments
2% lead
0.5% chromium

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>	<u>Leachate Concentration (ppm)</u>
	Pb	19,870	1.2
	Cr	4,914	1.8

Other properties: High ingestion toxicity

13. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3661

Waste Name: Oil Sludge with solvent and paint from the manufacture of telephone and telegraph parts.

Quantity: 100,000 gallons/year (liquid)

Percent Analysis: 37.6% oil and paint
58.2% solvents

Flashpoint: 100°F

14. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3661

Waste Name: Caustic and paint waste from the manufacture of telephone switching equipment

Quantity: 39,000 gallons/year (liquid)

pH: 14.0

Percent Analysis: 7.6% sodium hydroxide
0.5% zinc

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>
	CN	200.0

Other Properties: High dermal toxicity, high ingestion toxicity

15. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 371

Waste Name: Caustic Cleaning Waste from spray booth--paint stripping operations

Quantity: 66,000 gallons/year (liquid)

Percent Analysis: 13.3% sodium hydroxide
44.7% water

pH: 12.5

Other properties: High dermal toxicity

16. State: Illinois

Source: Waste Disposal Applications, Illinois EPA

SIC: 3312

Waste Name: Paint sludge from steel manufacturing

Quantity: 8,000 gallons/year (liquid)

Percent Analysis: 82.8% paint thinners

Flashpoint: 85°F

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>	<u>Leachate Concentration (ppm)</u>
	Pb	1015.0	6.8

Other properties: High ingestion toxicity

17. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3713

Waste Name: Paint sludge from manufacture of truck and tractor cabs

Quantity: 17,600 gallons/year (semi-solid)

Percent Analysis: 61.0% paint pigments
21.0% thinner
18.0% water

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>	<u>Leachate Concentration (ppm)</u>
	Pb	58,200	28
	Cr	8,370.0	0.1

Other properties: High ingestion toxicity

18. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3442

Waste Name: Paint waste from production of aluminum screens and doors

Quantity: 17,000 gallons/year (semi-solid)

Percent Analysis: 62.4% paint thinners

Flashpoint: 70°F

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>
	Cr	322.6

19. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3443

Waste Name: Paint and thinners from water heaters and
steel drums

Quantity: 20,000 gallons/year (liquid)

Percent Analysis: 62.4% paint thinners
0.3% chromium
1.7% lead
0.8% copper

Flashpoint: 70°F

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>	<u>Leachate Concentration (ppm)</u>
	Cr	2,975.0	0.2
	Pb	17,393.0	182.6

20. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 2431

Waste Name: Paint pigment sludge from window from manufacturing

Quantity: 27,500 gallons/year (semi-solid)

Percent Analysis: 50% polyured resin
15% xylene
5% cellosulde acetate
29.2% pigments

Flashpoint: 80°F

Other properties: High dermal and ingestion toxicity

21. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3579

Waste Name: Waste paint sludge from the manufacture of office copying machines

Quantity: 11,000 gallons/year (liquid)

Percent Analysis: 74.6% solvents
25.1% pigments

Flashpoint: 70°F

Other properties: High dermal and ingestion toxicity

22. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3612

Waste Name: Dry paint solids from the manufacture of stores and refrigerators

Quantity: 6,600 gallons/year (solid)

Percent Analysis: 15.7% high boiler solvent
84.3% paint pigments

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>
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	Pb	449.9
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Other properties: High ingestion toxicity

23. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 2552

Waste Name: Paint sludge from the manufacture of steel office furniture

Quantity: 150,000 gallons/year (semi-solid)

Percent Analysis: 23.1% paint thinners
63% paint pigments

Flashpoint: 100°F

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>
	Pb	2649.0
	Cr	214.0

Other properties: High ingestion toxicity

24. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 2541

Waste Name: Paint sludge from the manufacture of store furniture

Quantity: 50,000 gallons/year (solid)

Percent Analysis: 85% polyester
7% solvents
8% pigments

Flashpoint: 73°F

Other properties: High ingestion toxicity

25. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 2792

Waste Name: Paint sludge from the manufacture of paint charts
and color cards

Quantity: 19,800 gallons/year (semi-solid)

Percent Analysis: 78% paint pigments
22% lacquer thinner

Flashpoint: 79°F

Other properties: High ingestion toxicity

26. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

SIC: 3352

Waste Name: Paint waste from the manufacture of aluminum coils,
plates, and sheets

Quantity: 33,000 gallons/year (semi-solid)

Percent Analysis: 51.9% pigments
29.5% paint solvents

Flashpoint: 90°F

Tetrachloroethylene is not listed as a waste constituent in these manifests, although it is a constituent of concern. The presence of this constituent is shown by its presence in significant levels in untreated wastewater in a study of 14 plants undertaken by EPA (1) (see Table 2). It is believed that tetrachloroethylene would be present in solid residues in substantially higher concentrations, since the solid

TABLE 2

PRIORITY POLLUTANTS IN WASTEWATER FROM INDUSTRIAL PAINTING(1)

	Number of Times Analyzed	Maximum Value (mg/l)
Cadmium	49	0.095
Chromium	50	101.0
Lead	50	103.5
Cyanides	41	63.0
Toluene	41	4.16
Tetrachloroethylene	41	52.0

residues are not diluted.

2. Wastewater Treatment Sludge

As described above, some generators send their process paint residues to wastewater treatment, where a sludge is generated. These sludges are expected to contain most (or all) of the contaminants found in the paints themselves. The particular constituents of concern are cadmium, chromium, lead, cyanides, toluene, and tetrachloroethylene, since as just shown, these constituents have been demonstrated to be present in significant concentrations in paint residues.

Additional data throwing some light on the constituent concentrations in these wastewater treatment sludges is presented in Table 2. This data shows the maximum concentrations of the constituents of concern in wastewater samples from 14 industrial plants performing various types of painting. This data shows chromium, lead, and cyanides present in substantial concentrations, and cadmium and the organic contaminants present in lesser concentrations. These constituents would probably be found in the treatment sludges, for the following reasons. The heavy metals are not degradable and so would be present in the sludge. Cyanides and toluene are biodegradable ordinarily only in low concentrations (although some toluene would probably volatilize and therefore would not be in the sludge).⁽⁶⁾ Tetrachloroethylene is subject in theory to biodegradation,⁽⁶⁾ and thus might be present in lesser concentrations in the sludge than the other constituents of

concern. However, each of these constituents would undoubtedly be present in the wastewater treatment sludge in higher concentrations than in the wastewater since the sludges that contain the toxic constituents removed from the wastewater are dewatered, and therefore, the constituents are concentrated, before disposal.

Finally, the constituents of concern are typically expected to be present in these wastes. Table 3 shows toxic constituents present in the raw materials used by the paint industry, and shows lead, chromium, cyanides, and toluene in very wide use. The use of cadmium is less prevalent, but it is still utilized by roughly 20% of paint manufacturers.

It should be noted that the Agency possesses data⁽³⁾ suggesting that a great many other toxic substances are present in these wastes, specifically the toxic constituents listed in the paint manufacturing listing background document. The Agency however presently lacks reliable data as to these constituents' concentrations in industrial painting wastes. Further information as to the presence and concentrations of additional toxic constituents in these wastes is solicited.

3. Migratory Potential of Waste Constituents

The Administrator has classified these two wastes as hazardous because the Agency has reason to believe that they contain substantial concentrations of the toxic raw materials used in the formulation of paint products and therefore that the wastes pose a substantial threat to human health and the environment. Specifically, these wastes are being listed as

TABLE 3

TOXIC CONSTITUENTS IN RAW MATERIALS
USED BY THE PAINT INDUSTRY(1)

Priority Pollutant	Responders Indicating Usage of Raw Materials Containing Specific Constituents of Concern			
	Minimum		Maximum	
	No. of Plants	Percent	No. of Plants	Percent
Cadmium	260	18.9	312	22.7
Chromium	1042	75.8	1083	78.8
Lead	833	60.6	1016	73.9
Cyanides	860	62.6	1064	77.4
Toluene	961	69.6	998	72.6

*Data generated from 1374 responses to paint industry "308" survey. Since many of the raw materials included in the "308" Data Collection Portfolio can contain more than one toxic pollutant, the Agency was unable to obtain unambiguous counts for the occurrence of particular toxic pollutants. A conservative approach was taken because of this. When the Data Collection Portfolio response did not indicate clearly which toxic pollutant was in use, the Agency made two counts - one including neither, one including both. This gave a maximum and minimum count for toxic pollutants. Twenty-eight plants did not check any boxes in the survey. It is not clear whether the respondents use none of the listed raw materials or whether they did not fill out the questionnaire completely. Finally, within the group of respondents to the raw materials survey, it was found that each raw materials question was answered positively at least once. This indicates that the raw materials questions represented appropriate paint raw materials.

hazardous because of the presence of the following toxic constituents:

cadmium

chromium

lead

cyanides

toluene

tetrachloroethylene

Of these constituents, hexavalent chromium and tetrachloroethylene have been identified by the Agency's Carcinogen Assessment Group as possessing substantial evidence of carcinogenicity, increasing Agency concerns as to the potential of these wastes to cause substantial harm if mismanaged. Cadmium, lead and cyanides are highly toxic to man and toluene is moderately toxic by ingestion and inhalation. Under these circumstances, the Agency requires assurance that waste constituents will not migrate from the waste and persist should mismanagement occur, if the wastes are not to be listed as hazardous. Such assurance does not appear possible here since as shown below, all of the waste constituents appear quite capable of migration in substantial concentrations, and of mobility and persistence upon environmental release.

Toluene and tetrachloroethylene are relatively water soluble (toluene - 470 mg/l at 25°C, (4) tetrachloroethylene -

150 mg/l at 25°C⁽⁸⁾). The heavy metals are likewise known to be capable of migration, as shown by waste extraction data (see State Manifest Data Number 9, 10, 16, 17, 19). These compounds thus present a danger of migration via a groundwater exposure pathway if exposed to a leaching media.

Toluene and tetrachloroethylene are also significantly volatile (toluene - 28.4 mm at 25°C,⁽⁴⁾ tetrachloroethylene - 150 mm at 25°C⁽⁸⁾) and could pose an air inhalation hazard to environmental receptors in the vicinity of improperly disposed wastes.

These constituents are likewise capable of mobility and persistence upon environmental release. Many constituents have in fact been involved in damage incidents resulting from improper waste management, empirically demonstrating their mobility and persistence. For example, among other contaminants, tetrachloroethylene was involved in the contamination of drinking water sources in New Hanover, North Carolina.⁽⁶⁾ Toluene and tetrachloroethylene are among the constituents present in water and air samples taken in the Love Canal area.⁽⁷⁾ Heavy metals and cyanides likewise have been involved in numerous damage incidents from improper waste disposal.⁽⁶⁾

These waste constituents thus have the capacity for migration, mobility and persistence, raising the possibility of potential hazard if the wastes are mismanaged.

Ground water or surface water contamination could result, for example, if sites are selected improperly i.e.(in areas with permeable soils) or if no leachate control measures are utilized. Lagoon-disposed wastes (such as treatment sludges prior to dredging) also pose a potential for hazard because a large quantity of liquid is available to percolate through the solids and soil beneath the fill. Further, the Agency is also concerned that the lagooned wastes could contaminate surface waters if not managed to prevent flooding or total washout.

An additional consideration favoring hazardous waste status for these wastes is that they are transported to off-site disposal facilities. This increases the likelihood of their being mismanaged, i.e., uncontrolled transportation may result either in their not being properly handled during transport or their not reaching their destination at all. A transportation and manifest system combined with designated standards for the management of these wastes will greatly reduce their availability to harm to humans and the environment.

V. Health and Environmental Effects (9)

The following contaminants of paint wastes are designated as priority pollutants under Section 307(a) of the Clean Water Act:

- cadmium
- chromium
- lead
- cyanides
- toluene
- tetrachloroethylene

Lead is also regulated under the Clean Air Act. Proposed or final standards have been issued for most of these chemicals under the Occupational Safety and Health Act of 1970. EPA's Carcinogen Assessment Group (CAG) has evaluated several constituents of these waste streams and found sufficient evidence to indicate that chromium (Cr⁺⁶) and tetrachloroethylene are carcinogens. More specific information on the health effects of these chemicals are summarized below. Additional information on the adverse health and environmental effects of these constituents can be found in Appendix A.

Cadmium

Cadmium is an extremely dangerous cumulative toxicant, causing progressive chronic poisoning in mammals, fish, and probably other organisms. The metal is not excreted.

Toxic effects of cadmium on man have been reported

from throughout the world. Cadmium may be a factor in the development of such human pathological conditions as kidney disease, testicular tumors, hypertension, arteriosclerosis, growth inhibition, chronic disease of old age, and cancer. Cadmium is normally ingested by humans through food and water as well as by breathing air contaminated by cadmium dust. Cadmium is cumulative in the liver, kidney, pancreas, and thyroid of humans and other animals. A severe bone and kidney syndrome known as itai-itai disease has been documented in Japan as caused by cadmium ingestion via drinking water and contaminated irrigation water. Ingestion of as little as 0.6 mg/day has produced the disease. Cadmium acts synergistically with other metals. Copper and zinc substantially increase its toxicity.

Cadmium is concentrated by marine organisms, particularly molluscs, which accumulate cadmium in calcareous tissues and in the viscera. A concentration factor of 1000 for cadmium in fish muscle has been reported, as have concentration factors of 3000 in marine plants and up to 29,600 in certain marine animals. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, and crustaceans appear to be more sensitive than fish eggs and larvae.

For the protection of human health from the toxic properties of cadmium ingested through water and through

contaminated aquatic organisms, the ambient water criterion is determined to be 0.010 mg/l.

Data show that cadmium can be incorporated into crops, including vegetables and grains, from contaminated soils. Since the crops themselves show no adverse effects from soils with levels up to 100 mg/kg cadmium, these contaminated crops could have a significant impact on human health. Two Federal agencies have already recognized the potential adverse human health effects posed by the use of sludge on cropland. The FDA recommends that sludge containing over 30 mg/kg of cadmium should not be used on agricultural land. Sewage sludge contains 3 to 300 mg/kg (dry basis) of cadmium; mean = 10 mg/kg; median = 16 mg/kg. The USDA also recommends placing limits on the total cadmium from sludge that may be applied to land.

Chromium

The two chromium forms most frequently found in industry wastewaters are hexavalent and trivalent chromium. Some of it is reduced to trivalent chromium as part of the process reaction. The raw wastewater containing both valence states is usually treated first to reduce remaining hexavalent to trivalent chromium, and second to precipitate the trivalent form as the hydroxide. The hexavalent form is not removed by lime treatment.

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled, and induces skin

sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Hexavalent chromium is a known human carcinogen. Levels of chromate ions that show no effect in man appear to be so low as to prohibit determination, to date.

The toxicity of chromium salts to fish and other aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially the effect of water hardness. Studies have shown that trivalent chromium is more toxic to fish of some types than is hexavalent chromium. Hexavalent chromium retards growth of one fish species at 0.0002 mg/l. Fish food organisms and other lower forms of aquatic life are extremely sensitive to chromium. Therefore, both hexavalent and trivalent chromium must be considered harmful to particular fish or organisms.

For the protection of human health from the toxic properties of chromium (except hexavalent chromium) ingested through water and contaminated aquatic organisms, the recommended water quality criterion is 0.050 mg/l. For the maximum protection of human health from the potential carcinogenic effects of exposure to hexavalent chromium through ingestion of water and contaminated aquatic organisms, the ambient water concentration is zero.

Chromium is not destroyed when treated by wastewater treatment (although the oxidation state may change), and will either pass through to the wastewater treatment effluent or be

cyanide.

The toxic mechanism of cyanide is essentially an inhibition of oxygen metabolism, i.e., rendering the tissues incapable of exchanging oxygen. The cyanogen compounds are true noncumulative protoplasmic poisons. They arrest the activity of all forms of animal life. Cyanide shows a very specific type of toxic action. It inhibits the cytochrome oxidase system. This system is the one which facilitates electron transfer from reduced metabolites to molecular oxygen. The human body can convert cyanide to a non-toxic thiocyanate and eliminate it. However, if the quantity of cyanide ingested is too great at one time, the inhibition of oxygen utilization proves fatal before the detoxifying reaction reduces the cyanide concentration to a safe level.

Cyanides are more toxic to fish than to lower forms of aquatic organisms such as midge larvae, crustaceans, and mussels. Toxicity to fish is a function of chemical form and concentration, and is influenced by the rate of metabolism (temperature), the level of dissolved oxygen, and pH. In laboratory studies free cyanide concentrations ranging from 0.05 to 0.15 mg/l have been proven to be fatal to sensitive fish species including trout, bluegill, and fathead minnows. Levels above 0.2 mg/l are rapidly fatal to most fish species. Long term sublethal concentrations of cyanide as low as 0.01 mg/l have been shown to affect the ability of fish to function normally, e.g., reproduce, grow, and swim.

For the protection of human health from the toxic properties of cyanide ingested through water and through

contaminated aquatic organisms, the ambient water quality criterion is determined to be 0.200 mg/l.

Tetrachloroethylene

Tetrachloroethylene is highly toxic via ingestion and moderately toxic via inhalation and skin absorption as well as being carcinogenic. Tetrachloroethylene has a vapor pressure of 19 mm Hg at 20°C. It is insoluble in water but soluble in organic solvents. Because tetrachloroethylene is volatile disposal of this waste in an uncontrolled manner poses risks to human health by all routes of exposure.

The principal toxic effect of tetrachloroethylene on humans is central nervous system depression when the compound is inhaled. Headache, fatigue, sleepiness, dizziness and sensations of intoxication are reported. Severity of effects increases with vapor concentration. High integrated exposure (concentration times duration) produces kidney and liver damage. Very limited data on tetrachloroethylene ingested by laboratory animals indicate liver damage occurs when PCE is administered by that route. Tetrachloroethylene tends to distribute to fat in mammalian bodies.

One report found in the literature suggests, but does not conclude, that tetrachloroethylene is teratogenic. Tetrachloroethylene has been demonstrated to be a liver carcinogen in B6C3-F1 mice.

For the maximum protection of human health from the

potential carcinogenic effects of exposure to tetrachloroethylene through ingestion of water and contaminated aquatic organisms, the ambient water concentration is zero. Concentrations of tetrachloroethylene estimated to result in additional lifetime cancer risk levels of 10^{-7} , 10^{-6} , and 10^{-5} are 0.000020 mg/l, 0.00020 mg/l, and 0-.0020 mg/l, respectively.

Toluene

Toluene is moderately toxic by ingestion and inhalation. Because toluene is both water soluble and volatile, it may pose a threat to human health by both exposure routes, respectively. Toluene is volatile (vapor pressure of toluene is 36.7 mm at 30°C); handling and disposal of the waste may thus pose an inhalation hazard. If the waste is disposed in an unsecured landfill the toluene may be solubilized from the waste (the water solubility of toluene is 535 mg/l, and it is miscible with a variety of organic solvents) by rainfall and contaminate underlying potable groundwater sources with may pose a hazard to human health when the water is ingested.

Most data on the effects of toluene in human and other mammals have been based on inhalation exposure or dermal contact studies. There appear to be no reports of oral administration of toluene on human subjects. A long term toxicity study on female rats revealed no adverse effects on growth, mortality, appearance and behavior, organ to body weight ratios, blood-urea nitrogen level, bone marrow counts, peripheral blood counts, or morphology of major organs. The effects of inhaled

toluene on the central nervous system, both at high and low concentrations, have been studied in humans and animals. However, ingested toluene is expected to be handled differently by the body because it is absorbed more slowly and must first pass through the liver before reaching the nervous system. Toluene is extensively and rapidly metabolized in the liver. One of the principal metabolic products of toluene is benzoic acid, which itself seems to have little potential to produce tissue injury.

Toluene has been found in fish caught in harbor waters in the vicinity of petroleum and petrochemical plants. Bioconcentration studies have not been conducted, but bioconcentration factors have been calculated on the basis of the octanol-water partition coefficient.

For the protection of human health from the toxic properties of toluene ingested through water and through contaminated aquatic organisms, the ambient water criterion is determined to be 12.4 mg/l.

REFERENCES

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4. Karel Verschueren, Handbook of Environmental Data on Organic Chemicals, Copyright 1977, Litton Educational Publishing.
5. U.S. EPA, Office of Solid Waste, Open Files--State Manifest Data, 1980.
6. Resource Losses from Surface Water, Groundwater, and Atmospheric Contamination: A Catalog; prepared by the Environment and Natural Resources Policy Division of the Congressional Research Service of the Library of Congress for the Senate Committee on Environment and Public Works, Serial No. 96-9, 96th Congress, 2nd Session (1980).
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8. Gosselin, Rober E., et al, Clinical Toxicity of Commercial Products, Fourth Edition, The Williams and Wilkin Company, Baltimore, 1976.
9. U.S. EPA, Effluent Guidelines Division, Development Document for Effluent Limitations Guidelines and Standards for Foundries Metal Molding and Casting Point Source Category, Section VI--Pollutant Parameters, April 1980.

VI. Response to Comments to the Proposed Rule

Several commenters responding to the proposed Hazardous Waste Guidelines and Regulations (43 FR 58946, December 18, 1978) objected to the category "paint wastes" which appeared in §250.14(a) as a hazardous waste. The main objection was that the category was overly broad. In response, EPA has been more specific in its listing of paint wastes. The two wastes listed in this document are generated by a number of industries engaged in industrial painting. As EPA obtains more information on paint wastes, additional generic categories may be added to the hazardous waste list.

Inorganic Chemicals

LISTING BACKGROUND DOCUMENT

CHLORINE PRODUCTION

BRINE PURIFICATION MUDS FROM THE MERCURY CELL PROCESS
IN CHLORINE PRODUCTION WHERE SEPARATELY PREPURIFIED
BRINE IS NOT USED (T).

WASTEWATER TREATMENT SLUDGES FROM THE MERCURY CELL
PROCESS IN CHLORINE PRODUCTION (T).*/

I. SUMMARY OF BASIS FOR LISTING

The solid wastes of concern in this document are muds from brine purification and wastewater treatment sludges from the mercury cell process in chlorine production. The toxic constituent of concern in these wastes is the heavy metal mercury.

The Administrator has determined that mercury-bearing sludges and muds resulting from the mercury cell process in chlorine production 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 which 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 generated in large quantities and contain significant concentrations of mercury. At the present time approximately 42,000 kkg of hazardous mercury-bearing wastes are generated each year. These wastes are calculated to contain about 600 kkg of mercury. Large quantities of this highly toxic pollutant are thus available for environmental release.
2. These wastes have been involved in a number of serious damage incidents, demonstrating empirically that improper waste management may result in substantial environmental hazard.

*/ This waste stream was not included in the initial listing, and is being initially proposed in the present document.

II. SOURCES OF THE MERCURY AND TYPICAL DISPOSAL PRACTICES

A. Industry Profile

Twenty-seven facilities, located in 16 states, are engaged in chlorine and either sodium hydroxide or potassium hydroxide manufacture using the mercury cell process.^(1,2) These facilities are identified in Tables 1 and 2. In 1979, their mercury cell production capacity was reported as ranging from 36,000 to 272,000 kkg per year.⁽²⁾

B. Manufacturing Process (Modified from Reference 1)

In the mercury cell process, rock or evaporated salt is dissolved in recycled brine or in fresh water in agitated tanks to form a saturated salt brine. In plants, not using prepurified salt--most of the plants using this process--^{*/} this brine is purified by adding soda ash and sodium hydroxide, and in some cases barium salts, precipitating barium sulfate, and calcium and magnesium impurities of the salt as the carbonate and hydroxide, respectively. These are removed by settling and filtration; these filtered muds (A in Figure 1) constitute one of the wastes of concern. The purified brine is then fed to the electrolytic mercury cells, where it is decomposed

^{*/} Six facilities (listed in Table 2) use evaporated rock salt already purified in on-site diaphragm cell operations; these plants do not perform significant purification, and therefore do not generate mercury-containing brine muds.

TABLE 1

FACILITIES PRODUCING MERCURY-BEARING BRINE PREPARATION/PURIFICATION MUDS.

STATE	FACILITY	ROCK SALT SOURCE	CHLORINE CAPACITY 10 ³ kkg/yr (2)	HAZARDOUS BRINE MUDS	
				/CHLORINE CAPACITY (kg/kkg) (10,1)	TOTAL, DRY BASIS (kkg/year)
Alabama	Diamond Shamrock, Mobile	Louisiana	38	10	380
	Diamond Shamrock, Mus.Sho.	Louisiana	142	10	1,420
	Stauffer Chem., LeMoyne	Louisiana	50	10	500
Delaware	Diamond Shamrock, Del.City	New York	139	20	2,775
Georgia	Linden Prods., Brunswick	Louisiana	98	10	980
	Olin Corp., Augusta	Louisiana	100	10	1,000
Illinois	Monsanto Co., Sauget	Kansas	40	20	800
Kentucky	B.F.Goodrich, Calvert City	Louisiana	116	10	1,160
	Pennwalt Corp., " "	Ohio	109	30	3,265 (c)
Louisiana	Stauffer Chem., St.Gabriel	Louisiana	150	10	1,500
Maine	International Minerals, Orrington	New York	72	20	1,440 (c)
New Jersey	Linden Products, Linden	New York	131	20	2,620 (c)
New York	Hooker Sobin, Niag. Falls	New York and Sask.KCl(b)	59	25	1,474
	Olin Corp., Niag. Falls	New York	80	20	1,600
No. Carol.	Linden Products, Acme	Louisiana	54	10	540
Ohio	International Minerals, Ashtabula	Sask. KCl	36	30	1,088 (c)
Tennessee	Olin Corp., Charleston	Tennessee	227	30	6,803
Texas	Alcoa, Point Comfort	Louisiana	153	10	1,530
Washington	Georgia Pacific, Bellingham	Prepurif. evap.	83	0.7	58
West Va.	Linden Products, Moundsville	W.Va.	87	45	3,918
Wisconsin	BASF Wyandotte, Port Edwards	Michigan	64	45	3,020 (c)
			2028		37,871

- a) The amounts of hazardous brine muds generated were calculated by multiplying the plant annual capacity (Reference #2) by the amount of brine muds generated per kkg of chlorine produced.
- b) This facility uses New York rock salt and Saskatchewan potassium chloride salt in approximately equal proportions. These salts generate 20kg and 30 kg of hazardous brine muds respectively per metric ton of chlorine produced. An average value of 25 kg was used.
- c) These facilities segregate the two waste streams A and B of Figure 1.

Table 2

FACILITIES WHICH DO NOT PRODUCE MERCURY-BEARING BRINE MUDS.(a)

STATE	FACILITY	MERCURY CELL CHLORINE CAPACITY 10 ³ kkg/yr ^(b)	SALT SOURCE
Alabama	Olin Corp., McIntosh	163	Black Warrior
Louisiana	BASF Wyandotte Corp., Geismar	136	Louisiana
	PPG, Lake Charles	272	Louisiana
New York	Linden Products, Syracuse Syracuse(c)	59	New York State
Texas	Diamond Shamrock, La Porte	181	Louisiana
West Va.	PPG, Natrium	109	West Virginia
		920	

(a) These facilities use pure salt obtained from on-site diaphragm cell operations. No hazardous brine brine preparation/purification muds are generated at these plants because no purification step is needed.

(b) Information from Versar, Inc. files.

(c) Since 1970, this facility has been using pure salt from diaphragm cell operations. However, prior to 1970 brine purification operations were conducted in the mercury cell circuits so that some of the accumulated wastes from this site may be hazardous.

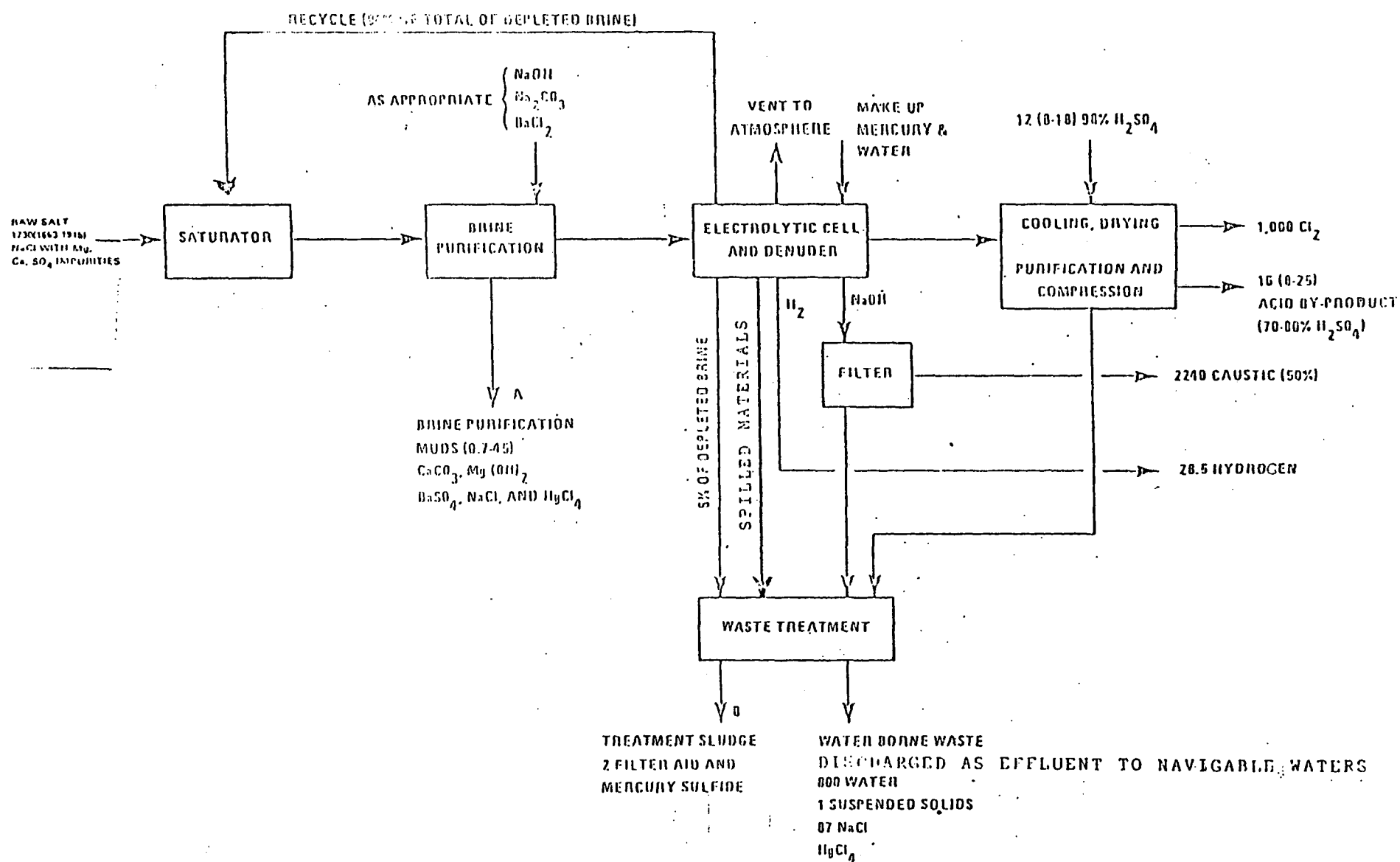


FIGURE 1 CHLOR-ALKALI MANUFACTURING BY MERCURY (1)

by electrolysis to produce chlorine and sodium amalgam. The spent brine from the mercury cells is dechlorinated and approximately 94% is returned (recycled) to the initial brine make-up for resaturation; the remainder is discharged to wastewater treatment.

Since some of the feed of the brine purifier is a mercury bearing recycle stream from the electrolytic cell, the muds (A in Figure 1) resulting from brine purification are contaminated with mercury.

In all plants, the depleted purged brines from the electrolytic cell, together with two other waste streams generated from ancillary processes, are channeled to waste treatment. Wastewater treatment generates sludges (B in Figure 1) in amounts averaging 2 kg of sludge per kkg of chlorine product.⁽¹⁾ These wastes, which contain about 15%* mercury (as mercuric sulfide) constitute the second waste of concern.**

The mercury leaving the cells in the form of sodium mercury amalgam is sent to denuders where the amalgam is decomposed at 80°C by the addition of deionized water. Water reacts with the sodium mercury amalgam to produce a 50 percent solution of sodium

*This conclusion is estimated from the following factors:

- (1) approximately 52 kkg of brine are used per kkg of chlorine produced⁽³⁾; about 3100 kg (6%, Figure 1) are purged⁽¹⁾. These brines contain about 20 ppm of mercury⁽³⁾. Thus, $3,100 \text{ kg brines/kkg Cl}_2 \times 20 \times 10^{-6} \text{ kg mercury/kg brine} = 0.06 \text{ kg mercury}$. Since these are crude estimates, this figure is rounded to 0.1.
- (2) It is estimated that about 0.3 kg of mercury are spilled per kkg of chlorine produced.⁽²³⁾
- (3) It is estimated that about 1.7 kkg of filter residues and occluded water are generated per kkg of chlorine produced.

Thus the treatment sludges total about 2.0 kg per kkg of chlorine; of this total 0.3 kg, or 15%, is mercury contaminated.

**The waterborne waste stream does not contain sufficient mercury to be of regulatory concern.

hydroxide* essentially free of sodium chloride. This solution is filtered to recover entrained mercury. The waste from the filtration step is sent to wastewater treatment, where mercury precipitates into the treatment sludge (stream B). Entrained mercury is removed from the hydrogen generated in the denuders, and returned to the electrolytic process. After removal of mercury, the hydrogen is either compressed for sale, used on-site, or used as a fuel. The chlorine gas collected in the electrolytic cells is cooled to condense out excess water vapor. This stream, which is essentially free of mercury, is sent to waste treatment. The partially dried chlorine is then scrubbed with 98 percent sulfuric acid to remove the rest of the entrained water vapor and is collected, compressed and liquified.

C. Waste Generation

The wastes of interest in this document are muds that result from the treatment of rock salt and recycled depleted brine, and sludges generated by the treatment of purged, depleted brines and ancillary waste streams. Twenty one facilities generate both of these wastes. Six other facilities, (those which use prepurified salt) do not generate brine purification muds (waste A, Figure 1).

*Potassium hydroxide is produced in plants using potassium chloride as raw material.

The source of mercury in the brine purification muds is the recycled brine from the electrolytic cell (which mercury is removed in the purification process step).

These brine preparation muds contain substantial concentrations of mercury, either in elemental form or as the complex ion, HgCl_4^- . Available data, in fact, indicate that the concentration of mercury in these muds ranges from 500(12) to 2000 ppm (13,14) of mercury. Total potential mercury loadings are likewise substantial: the 38,000 tons of hazardous brine preparation and purification muds generated each year (Table 1) are calculated to contain 19 to 76 kkg of mercury.

It should be noted that the amount of muds produced depends on the source of the salt used as raw material.(11,12) As indicated in Table 1, facilities using salt from the Texas-Louisiana salt dome generate about 10 kg of brine mud per kkg of chlorine. Plants using other salt sources generate brine muds in amounts ranging from about 20 kg per kkg of chlorine (salt from Kansas and New York) to 45 kg per kkg of chlorine (salt from Michigan and West Virginia deposits). All the above quoted figures are on a dry-weight basis.(1,10,11,12)

The sludges resulting from wastewater treatment consist mainly of mercuric sulfide. Approximately 4,300*

*Calculated from mercury cell chlorine production data for 1977(3) and treatment sludge data in Figure 1: 2128×10^3 kkg chlorine produced/year \times 2 kkg sludge waste/ 10^3 kkg chlorine = 4256 kkg sludge waste.

kg of this waste containing 15% mercuric sulfide (equivalent in total to 645 kg of mercury) are generated each year.

Therefore, a total of approximately 42,000 kg of hazardous mercury-bearing wastes containing as much as 620 kg of mercury are generated annually from the mercury cell process. This estimate is reasonable in view of the reported 846 kg of mercury lost to the environment as wastes and air emissions for this industry in 1965.(15)

D. Waste Management (1,11,12)

Of the 21 plants generating both listed waste streams, all but five combine their wastes prior to treatment. One plant retorts all mercury-containing wastes, eight others retort only the mercury-rich wastes, and of these eight, four store these wastes in drums until decisions are made on final disposal. One plant sends sludges to contractors for recovery. This latter disposal method is occasionally used by other facilities. Nine plants now use on-site pond storage of sludges, and seven use on-site landfill. Four plants send wastes to contractors for secured landfilling. Several plants employ combinations of these treatment and disposal techniques.* /

* / One plant utilizes a relatively new system for recovery of mercury from virtually all mercury bearing wastes. Treatment of contaminated wastes with sodium hypochlorite leaves wastes with a residual mercury content of less than 40 ppm. This treated waste is then disposed of by landfilling. This waste recovery process is capable of treating both brine mud and treatment sludges, and of recycling recovered mercuric chloride. However, its applicability is limited by cell design and water balance considerations.

II. DISCUSSION OF BASIS FOR LISTING

A. Hazards Posed by the Waste

The two listed wastes are of regulatory concern because of their contamination with the toxic heavy metal mercury. Brine preparation and purification muds are reported to contain as much as 2000 ppm of mercury, and treatment sludges contain about 15.0% mercury. Moreover, very large amounts of these wastes (42,000 kkg) are generated. Mercury is highly toxic to a wide variety of organisms, including man, and can accumulate in biological organisms in its various forms.

These wastes have been involved in a number of damage incidents, demonstrating empirically that improper management of these wastes may cause substantial harm. These damage incidents are described below.

- The Olin 102nd Street Landfill, Niagara Falls, Niagara County, New York.(4)

From mid 1948 to September, 1970 Olin Chemical Corporation utilized a landfill for the disposal of chemical wastes from its Niagara Falls plant. These wastes include brine sludge from a mercury cell chlor-alkali plant plus other wastes such as chlorinated organics, lime wastes, WWH wastes, fly ash, black cake wastes (sodium chloride, sodium chlorite, sodium chlorate, carbon, calcium carbonate, calcium hydroxide), graphite from electrolytic cells and concrete cell bodies, together

with a limited amount of research materials. This landfill is located in a suburban section of Niagara Falls, New York, contiguous to the northern shore of the Niagara River. When it was closed, the landfill was "secured" by covering the waste with a soil cover, establishing vegetation, and by constructing a dike along the Niagara River.

In 1978, a surface and groundwater sampling program was initiated at the landfill site by RECRA Research Inc. and WEHRAN Engineering Corporation⁽³⁾ to provide both baseline water quality data and sufficient information to assess the impact of previous disposal operations at the site. The program included the analysis of waters from the various groundwater regimes encountered on site, and of grab samples of surface waters from the Niagara River. In view of the fact that the EPA National Interim Primary Drinking Water Standard for mercury is 2 ug/l, pertinent results indicated serious mercury contamination:

- 1) On one of the two dates on which samples were taken, all readings for the six Niagara River surface grab samples (taken downstream from the furthest upriver point where the landfill borders the river) contravened the Drinking Water Standard in every case, with values ranging from 4.7 to 15 ug/l. On the second date, there was no significant

difference in concentrations up- and down stream from the landfill site. On this date, stormy conditions prevailed, and the river flow was much above normal.

- 2) Water samples were taken from the fourteen piezometers located in the saturated water zone in the landfill. Soluble mercury readings ranged from non-detectable values to 40 ug/l, with the bulk of the readings ranging from 3.9 ug/l to 11 ug/l. Out of 14 samples taken, 13 contravened the Drinking Water Standard.
- 3) Contiguous to the saturated water zone of the landfill is a semi-confined aquifer of alluvial deposits. Water samples were taken from piezometers located in the alluvial deposits aquifer. Soluble mercury readings ranged from non-detectable to 35 ug/l. These data are believed to indicate that leachate from the landfill has migrated to this zone.

The Newco Solid Waste Management Facilities, Niagara Falls, New York (5,6)

At this disposal site, Olin is currently disposing of brine sludges emanating from its mercury chlor-alkali process. (This site has been used as a waste disposal area for over 80 years.) An evaluation was performed of the presence, movement, and quality of groundwater at this facility, and the data were incorporated in a Draft Environmental Impact Statement for the State of

New York.(5,6) Elevated levels of mercury (6.6 ug/l) have been found in the leachate of mercury-contaminated sludges that have been disposed of in the landfill.

- In another damage incident(16) (involving an inactive chloralkali facility not otherwise identified in the literature), leaching of mercury from the solid wastes from the facility caused elevated levels of mercury in downstream water, suspended matter, and bottom sediment. About 39 kg of mercury are lost to water from this unlined lagoon each year. Concentration of mercury in water and suspended matter immediately downstream from the plant site are about 20 times higher than immediately upstream. The silt-clay fraction of bottom sediment immediately downstream of the plant site contains up to 200 times as much mercury as the similar sediments collected immediately upstream from this facility.(16)

- Contamination of Surface Water from an Alkali Processing Plant in Saltville, Virginia(21):

In another damage incident involving the Olin Corporation, an alkali processing plant generating the wastes listed in this document (and other industrial waste) disposed of these wastes in a series of lagoons located on the North Fork of the Huston River in Saltville, Virginia. Although the site (presently owned by Olin) ceased operating in 1972, wastes continue to leach from the disposal lagoons. Mercury

continues to enter the Holston River both from the site of the chlorine plant and from disposal lagoons used for disposal of chlorine production wastes. The grounds where the cell building once stood are estimated to contain some 220,000 lbs. of mercury. Cleanup costs are estimated at \$32-\$40 million.

The incidents described, as stated, demonstrate that mercury will migrate from this waste in harmful concentrations and reach environmental receptors causing substantial harm unless proper management is assured.

There are also other factors which warrant listing these wastes as hazardous. Transportation of these wastes to off-site disposal facilities, a management practice utilized by several manufacturers, increases the likelihood of mismanagement of these hazardous wastes, for example, due to improper handling during transport, or failure to reach the intended destination. 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.

The quantity of these wastes generated is an additional factor of concern. As indicated above, these wastes are generated in large quantities (42,000 kkg of waste per year, containing 700 kkg of mercury). Under improper disposal conditions, large amounts of mercury are thus available for environmental release. The large quantities of this contaminant poses the danger of polluting large areas of ground and surface waters.

Contamination will also occur over long periods of time, since elemental mercury persists indefinitely. Since large amounts of pollutants are available for environmental loading, the 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 environmental exposure to the harmful constituents in the wastes.

B. Health and Ecological Effects

The various forms of mercury are interconvertible under most environmental conditions. They are toxic to a wide variety of organisms, including man,⁽⁹⁾ and are known to accumulate in biological organisms.⁽⁹⁾ In humans, mercurials have been associated with neurological disorders, sensory impairment and tremors. Prenatal exposure can result in impaired brain development and psychomotor disorders. Organic mercury compounds inhibit fertility, and are more toxic than inorganic forms; 0.1 ug mercury/l is toxic to freshwater crayfish.⁽¹⁷⁾ Mercury is bioconcentrated 63,000-fold in fathead minnows foraging under laboratory conditions resembling those in the field.⁽¹⁸⁾ EPA estimates 200 ug/day as the acceptable daily intake and, in 1973, recommended 2 ug/l as a drinking water standard⁽¹⁹⁾; in 1979 a ten-fold reduction was further recommended⁽²⁰⁾. EPA has also recommended fresh water criteria as follows: 0.064 ug/l for inorganic mercury and 0.016 ug/l for methyl mercury⁽¹⁹⁾. Additional

information on the adverse effects of mercury on human health and the environment are documented in Appendix A.

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CHLORINATED HYDROCARBON WASTE FROM THE PURIFICATION STEP
OF THE DIAPHRAGM CELL PROCESS USING GRAPHITE ANODES IN
CHLORINE PRODUCTION (T)

I. SUMMARY OF BASIS FOR LISTING

Chlorinated hydrocarbons are generated during production of chlorine in diaphragm cells with graphite anodes. Purification results in separation of the chlorinated hydrocarbon waste from the product. The Administrator has determined that this waste is a solid waste which may pose a substantial hazard to human health and the environment when improperly transported, treated, stored, disposed of or otherwise managed, and which 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 compounds chloroform, carbon tetrachloride, hexachloroethane, trichloroethane, tetrachloroethylene, dichloroethylene, and 1,1,2,2-tetrachloroethane. The Agency's Carcinogenic Assessment Group has found that chloroform, carbon tetrachloride, tetrachloroethylene and 1,1,2,2-tetrachloroethane exhibit substantial evidence of carcinogenicity.
2. Typical management practices include deep well injection and incineration. Landfilling has also been employed as a disposal method. If these practices are unregulated, hazardous substances could be released to the environ-

ment. Improper construction or operation of a deep well could cause leakage of the waste from the well into usable aquifers; inadequate incineration can result in the generation of highly toxic combustion products such as phosgene. Uncontrolled landfilling may result in migration of hazardous substances to air and ground and surface waters.

3. Most of these compounds have significant migratory potential and have proven mobile and persistent in actual damage incidents caused by improper waste management.

II. SOURCES OF WASTE AND TYPICAL DISPOSAL PRACTICES

A. Industry Profile

Chlorine is produced by electrolysis of brine. It is used in the pulp and paper industry, plastics, water treatment and manufacture of organic and inorganic chemicals. About 75 percent of all chlorine manufactured in the United States is produced by the diaphragm cell process.⁽¹⁾ Approximately 32 plants use diaphragm cells; of these, six plants that utilize graphite anodes generate chlorinated hydrocarbon contaminants.*⁽¹⁾ Locations and production capacities of the six are given in Table 1.⁽²⁾

B. Manufacturing Process^(1,3)

Brine is purified by precipitation of metals before being sent to the diaphragm cell. Separation of solids during

*Graphite anodes predominated in the past, but in recent years most plants have replaced them with metal anodes.

Table 1

FACILITIES GENERATING CHLORINATED HYDROCARBON BEARING WASTES

<u>PLANT/LOCATION</u>	<u>PRODUCTION CAPACITY 10³ KKG/YR</u>
ICI Americas Baton Rouge, LA	156
Dow Chemical Midland, Mich.	256
Vulcan Materials Denver City, Tex.	121
Champion Production Canton, N.C.	26
Pasedena, Tex	20
PGG Industries Barberton, Ohio	100

purification generates waste brine muds; the Agency has no data at this time to indicate that the brine muds are hazardous. The purified brine is heated, brought to saturation by the addition of salt and acidified. The saturated salt solution is then electrolyzed in the diaphragm cell to form chlorine, hydrogen and sodium hydroxide. Chlorine is liberated at the anode, and hydrogen and sodium hydroxide are produced at the cathode. Reaction of chlorine with carbonaceous materials in the graphite anode results in the presence of chlorinated hydrocarbon contaminants in the chlorine product.

The hydrogen is purified and either sold, vented to the atmosphere or burned. The salt solution, which has been decomposed to approximately half its original concentration, is partially evaporated to increase the sodium hydroxide concentration. During evaporation, most of the sodium chloride precipitates from the solution and is recovered in salt separators. After filtration and washing, the salt is recycled to initial brine preparation.

Chlorine is recovered from the cell and cooled to remove water and other impurities. The condensates are discharged or recycled to the brine purifier. After cooling, the chlorine gas is scrubbed with acid to remove residual water vapor. The gas is then compressed and cooled to -30°C to -45°C . At these temperatures the chlorine liquefies and is pumped to steel storage tanks. Some further purification is performed during the cooling and liquefaction process. The chlorinated hydrocarbon waste of concern is liquefied from the chlorine

gas stream during purification. Figure 1 illustrates the process.

The Agency is concerned that wastewaters from clean-out of the diaphragm cell and from caustic evaporation and salt recovery operations and sludges resulting from treatment of these wastewaters may also be hazardous because they contain significant amounts of lead. The Agency currently does not have sufficient information on the concentrations and the migratory potential of the lead in these wastes, but they may be listed as hazardous at some time in the future. Generators, however, must determine whether this waste is hazardous pursuant to §262.11 of the Subtitle C regulations.

C. Waste Generation and Management (4)

As mentioned previously, chlorinated hydrocarbon contaminants arise primarily from the reaction of chlorine with carbonaceous materials in the graphite anode. Reaction of chlorine with oils and greases in the equipment and other hydrocarbons present in the system also contributes slightly to the generation of these contaminants. The chlorinated hydrocarbon contaminants are liquified from the chlorine gas stream during purification in amounts up to 1 kg per kkg of chlorine product.

Management practices vary. Vulcan Materials Co. disposes of the chlorinated hydrocarbon waste by deep well injection, and ICI Americas Ltd. incinerates its waste.

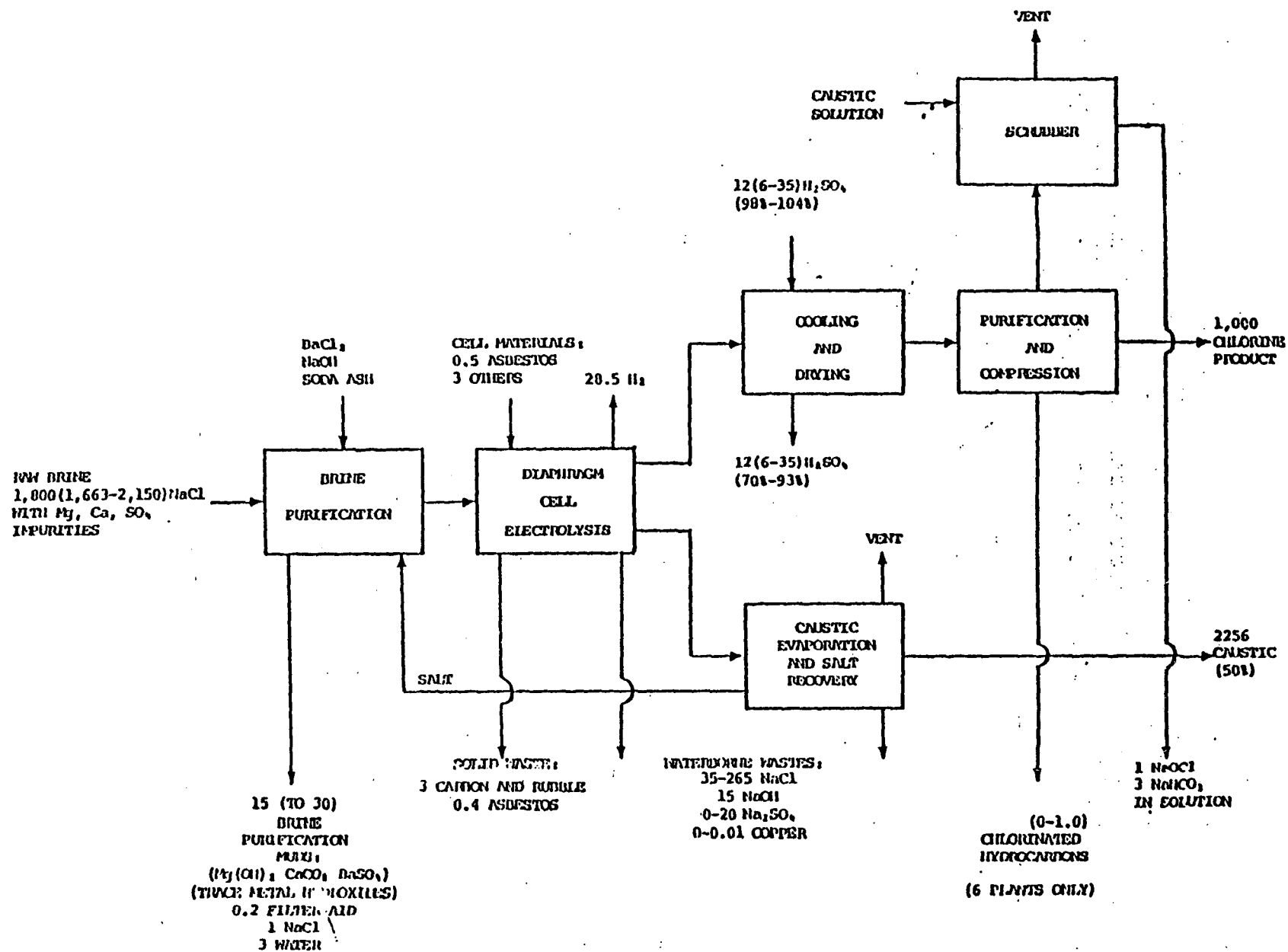


FIGURE 1. CHLOR-NAOH MANUFACTURE DIAPHRAGM CELL PROCESS /GRAPHITE ANODES (1).

Champion International Corp. and PPG Industries, Inc., which landfilled part of their wastes in sealed drums prior to 1977, apparently do not remove the chlorinated hydrocarbon contaminants from the chlorine product at this time. Dow Chemical's management practices are not known.

III. DISCUSSION OF BASIS FOR LISTING

A. Hazards Pose by the Waste

The constituents of the chlorinated hydrocarbon waste include the following (1):

<u>Compound Identified</u>	<u>Weight (%)</u>
chloroform	73.7
carbon tetrachloride	10.8
hexachloroethane	8.0
pentachloroethane	1.3
trichloroethane	1.0
tetrachloroethylene	0.6
dichloroethylene	0.3
1,1,2,2-tetrachloroethane	0.5

Clearly, the waste contains substantial amounts of organic compounds believed to be toxic and carcinogenic. Thus, in light of these constituents' high migratory potential and their ability to persist in the environment, improper management of this waste is likely to lead to substantial hazard.

Many of the constituents of concern have high vapor pressures and thus could pose a substantial hazard to human health and the environment via an air exposure pathway if the waste is improperly managed. Evidence available to

EPA's Carcinogen Assessment Group indicates that chloroform, carbon tetrachloride, a trichloroethane isomer, tetrachloroethylene, and 1,1,2,2-tetrachloroethane are carcinogenic. The Agency believes that the severity of the adverse health effects associated with exposure to these constituents provides a sound basis for listing the waste as hazardous. The high concentration of chloroform alone justifies the listing of this waste as hazardous, in the Agency's judgment. EPA's decision to list the waste is supported further by case histories which reveal that the hazardous constituents can migrate and persist in the environment.

Carbon tetrachloride, a major component of the waste, has been identified in school and basement air in the vicinity of Love Canal (8) and has been implicated in groundwater contamination incidents in Plainfield, Connecticut, where drinking water sources were adversely affected (9).

Chloroform has been found in drinking water wells near a Jackson Township, New Jersey landfill in which chemical wastes were dumped and is known to have migrated from the Love Canal disposal site (10). Hexachloroethane, another major constituent of the waste of concern, has also migrated from at least one chemical waste disposal site (Table 7.2, Ref. 9). In addition, damage incidents compiled by EPA reveal numerous instances of environmental contamination due to migration of trichloroethane and tetrachloroethylene.(10)

An estimated 75 kkg of waste per year is disposed of in deep wells or by incineration* (2); either method may unfavorably affect human health and the environment by contaminating ground and surface waters or polluting the atmosphere. A deep well injection system that is not properly designed or operated can release hazardous constituents from the well to aquifers used as drinking water sources. Improper incineration of chlorinated hydrocarbons can result in the generation and emission of highly toxic combustion products such as phosgene (5,6,7).

Landfilling of drummed waste has been practiced in the past. This disposal method presents obvious hazards; drums are likely to corrode in the landfill and release the waste to the surrounding area. Waste constituents could then volatilize and enter the atmosphere or migrate to ground and surface waters.

Health and Environmental Effects (From App. A unless otherwise noted.)

Chloroform

Chloroform has been identified by the EPA Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. Due to its highly volatile nature, (App. B), improper disposal of chloroform-containing wastes may pose an air pollution hazard. Long range exposures have caused

*This number was derived by multiplying 90% of the plant nameplate capacity by 0.5, on the assumption that, on average, 0.5 kg of chlorinated hydrocarbon wastes are generated per kkg of chlorine.

both physical and neurological disorders in humans, with liver and kidney toxic responses representing the most prevalent physical pathology. FDA prohibits the use of chloroform in drugs, cosmetics or food contact material. Additional information on this substance can be found in Appendix A.

Carbon Tetrachloride

Carbon tetrachloride (tetrachloromethane) has been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. Its toxic effects include neurological damage and damage to the kidney and lungs. It is volatile and highly soluble in water and is therefore expected to migrate readily in the environment (11). Additional information on carbon tetrachloride can be found in Appendix A.

Hexachloroethane

Hexachloroethane is moderately toxic to humans and is one of the more toxic chlorinated ethanes to aquatic species. It appears to have the potential to bioaccumulate (App. B). Humans exposed to hexachloroethane may suffer central nervous system depression and liver, kidney and heart degeneration. It has also been shown to be carcinogenic to laboratory animals. Little information is available on its environmental fate and transport, but, due to the nature of the adverse affects associated with exposure to this compound, the Agency believes that improper disposal of a waste containing a

significant amount of hexachloroethane may pose a hazard to human health and the environment. Additional information on hexachloroethane can be found in Appendix A.

Trichloroethane

The trichloroethanes (1,1,1-trichloroethane and 1,1,2-trichloroethane) are toxic to humans, animals and aquatic organisms and have been shown to be carcinogenic in laboratory animals. Due to the toxic and carcinogenic effects of these compounds, the Agency believes that improper management of wastes which contain them may pose a hazard to human health and the environment. Additional information on trichloroethanes may be found in Appendix A.

Dichloroethylenes

Exposure to dichloroethylenes can result in adverse human health effects. The three isomers appear to have similar toxic effects, including depression of the central nervous system and liver and kidney damage (App. A). Two isomers are mutagenic in bacterial systems and one isomer has been shown to be carcinogenic in laboratory animals (App. A). Information on environmental fate and transport is scarce but, due to the nature of the health effects resulting from exposure to dichloroethylenes, the Agency has determined that improper management of wastes containing these compounds poses a hazard to human health and the environment. Additional information on dichloroethylenes can be found in Appendix A.

Tetrachloroethylene

Tetrachloroethylene has been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. It is also toxic to aquatic species, and repeated exposure is implicated in mammalian liver and kidney damage (App.A). Little information is available concerning environmental fate and transport processes. Additional information on tetrachloroethylene is given in Appendix A.

1,1,2,2-Tetrachloroethane

1,1,2,2-tetrachloroethane has been identified by EPA's Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. Occupational exposure has produced neurological symptoms, liver and kidney damage, pulmonary edema and fatty degeneration of heart muscle. 1,1,2,2-tetrachloride is highly soluble in water (2900 ppm) and thus has high migratory potential (11). Although environmental fate and transport processes are not well-defined (microbial degradation appears to be the only known degradation mechanism (App. B), and this process is not likely to occur under the abiotic conditions prevailing in most aquifers), the Agency believes that, due to the severity of the health effects associated with exposure to this compound, improper disposal of the wastes in which it is contained poses a substantial hazard. See Appendix A for additional information.

The waste also contains a significant amount of pentachloroethane, a toxic chlorinated organic. At this time the Agency has not compiled data on specific health effects or environmental persistence and mobility; when the data are obtained, a document will be prepared for Appendix A.

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LISTING BACKGROUND DOCUMENT

TITANIUM DIOXIDE PRODUCTION

Wastewater Treatment Sludge From the Production of Titanium Dioxide Pigment Using Chromium Bearing Ores by the Chloride Process (T)

Summary of Basis for Listing

Process wastewaters from the production of titanium dioxide (TiO_2) by the chloride process contain oxides and chlorides of chromium and other metals that are present in the ore as contaminants. Treatment of these wastewaters prior to discharge generates a sludge that is usually discarded. The Administrator has determined that this wastewater treatment sludge 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. The waste contains significant quantities and concentrations of the toxic heavy metal chromium. It is estimated that more than 600 kkg of chromium are contained in the 800,000 kkg of these water treatment sludges produced each year, and that chromium concentrations in the sludge range from 500-12,000 ppm.
2. Chromium is capable of migrating from the waste if improper management occurs, and may be highly mobile upon release. Improper disposal of this waste thus may result in the release and migration of the chromium which may then contaminate ground or surface waters.
3. Five of the eight plants generating this waste currently dispose of their wastes in uncontrolled landfills ⁽¹⁾, thus posing a realistic possibility of migration of chromium to underground drinking

water sources. Further, chromium persists virtually indefinitely so that the danger of contamination is long-term should migration occur.

4. Very large quantities of this waste (800,000 kkg) are generated annually and are available for disposal as solid waste. There is thus greater likelihood of large scale contamination of the environment if the waste is not properly managed.

II. Sources of Waste and Typical Disposal Practices

A. Industry Profile

TiO₂ is a high volume chemical, ranking in the first fifty of U.S. chemicals production. More than fifty percent of the TiO₂ produced is used in paints, varnishes and lacquers. About one-third is used in the paper and plastics industries. Other uses are found in the manufacturing of ceramics, ink and rubber. About 610,000 kkg were produced in 1972.(2) It is manufactured by either the sulfate or chloride process; the latter accounts for 65% of production capacity (see Table 1). This document discusses the wastes generated by the chloride process, wastewater treatment sludge being the waste of concern.

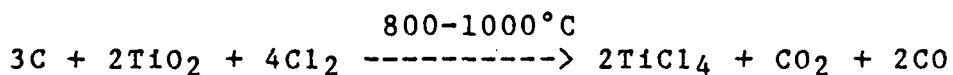
The chloride process uses rutile or upgraded ilmenite ores as raw materials. The chromium content of these ores varies considerably. Australian rutile typically contains 0.19% chromium oxide (6,7) and those ilmenite ores used in U.S. TiO₂ production (New York, Florida and Canadian ores) contain up to 0.15% chromium oxide.(6,7) However, the ores have been reported to contain as much as 4.0% chromium.(15)

Table 1 TITANIUM DIOXIDE PRODUCERS (CHLORIDE PROCESS)(1)

Manufacturer	Location	Capacity kkg/yr
E.I. DuPont de Nemours Co., Inc.	Antioch, California	27,200
	New Johnsonville, Tennessee	207,000
	Edgemoor, Delaware	99,000
Kerr-McGee Corp.	Hamilton, Mississippi	45,000
SCM Corporation Glidden-Durkee Division	Baltimore, Maryland	26,300
	Ashtabula, Ohio	24,500
New Jersey Zinc	Ashtabula, Ohio	27,200
American Cyanamid	Savannah, Georgia	<u>36,400</u>
Total		492,600

B. Manufacturing Process (1,8) (see Figure 1 for Flow Chart)

In the manufacturing process, the raw ore is first dried. Dried ore, dried coke and gaseous chlorine are then charged to a heated continuous fluidized bed chlorination reactor, converting the titanium oxide in the ore to titanium tetrachloride by the following reaction:



The gases leaving the chlorinator consist of titanium tetrachloride, unreacted chlorine, carbon dioxide, carbon monoxide and volatile heavy metal chlorides generated by the reaction of chlorine with metallic impurities in the ore. These gases are subjected to a purification step involving cooling, condensation, and separation of the heavy metal impurities, specifically the chlorides of vanadium, zirconium, chromium and other trace heavy metals, silicon, and titanium. This process stream is labeled "A" in Figure 1.

This purification step is of special importance for purpose of this document, because it is the point in the process where chromium enters the solid waste stream. More importantly, virtually all of the chromium impurities in the raw ore are removed at this point in the process and, as explained below, are therefore likely to be present in the wastewater treatment sludge. The residual uncondensed gases consisting of unreacted chlorine, hydrochloric acid, traces

data for solid content of various waste streams as composite information supplied by industry plants, based on 1974 production, and verified on a follow-up basis for accuracy through 1977;

*the quantity of chromium in waste stream A (as chromium chloride) is approximately the same regardless of ore type, due to the different quantities of each ore type required to produce the same quantity of product, and the differing percentages of chromium (as chromium oxide) in each type of ore.

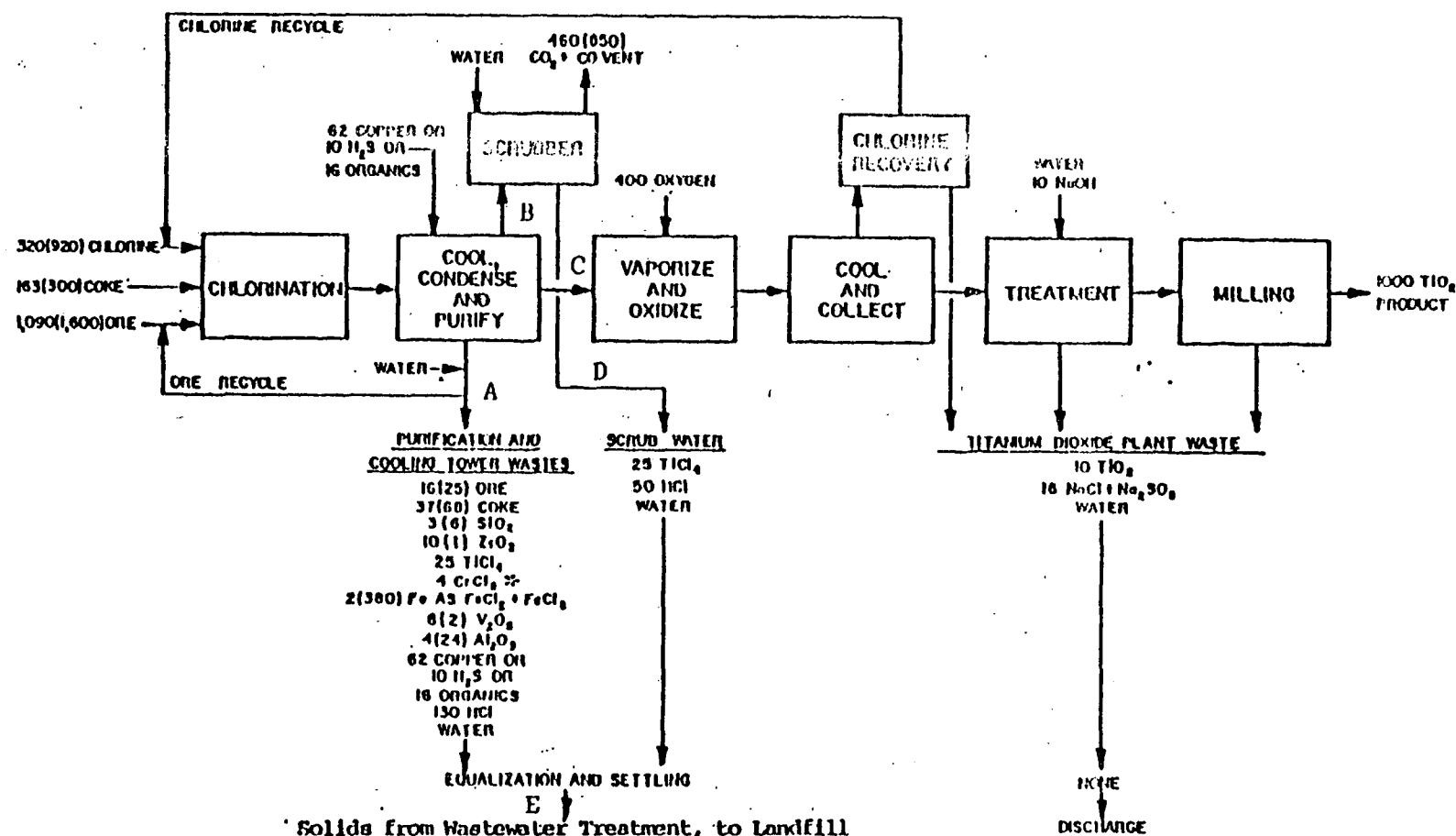


FIGURE 1
 TITANIUM DIOXIDE MANUFACTURE
 BY THE CHLORIDE PROCESS USING RUTILE ORE OR ILMENITE ORE *

NOTE: figures in parentheses are for ilmenite ores

of phosgene, carbon monoxide, carbon dioxide, titanium tetrachloride and nitrogen pass to the scrubber (stream B, Figure 1), where they are scrubbed (cleaned) by a two-step process. The waste resulting from this process is labelled "D" in Figure 1.

This stream (D) is not reported to contain chromium, this element having been removed by the purification step. The Agency believes, however, that trace amounts of chromium are present in this stream, but (as stated below) since this stream is combined with stream A prior to sludge generation, the fact is not of regulatory significance.

The remaining reactor condensate (stream C, Figure 1) is purified, vaporized and reacted in special burners with oxygen (or air) to form the product titanium dioxide:



The resulting gas-solid mixture is cooled to near ambient temperature, and the solid titanium dioxide is separated from the gas phase by proprietary dry collection methods. The residual gas stream is further cooled to recover chlorine, which is recycled to the chlorinator. The tail gases are released to the atmosphere after chlorine recovery is completed. ^{*/}

^{*/}There is a product washing step (labelled 'treatment' in Fig. 1) which deacidifies the product. A separate waste stream is generated at this point, which is not believed to be hazardous, and further is believed to contain only insignificant amounts of chromium.

C. Waste Generation

The waterborne waste streams A and D are typically combined (equalized) and neutralized, then lagooned to settle the suspended solids prior to effluent discharge.⁽⁸⁾ The resulting sludge (E in Figure 1) is the waste of concern in this document. Chromium is the waste constituent of concern. Chromium is present in the process wastewater mostly as the chloride (some unreacted Cr_2O_3 is also present), both predominantly as the trivalent species. When the wastewater is neutralized, chromium hydroxide is formed. Unreacted chromium chloride is expected to be entrained by the hydroxide precipitate. The relative concentrations of the two chromium compounds will depend in part on the efficiency of the neutralization step.

The Agency believes chromium concentrations in the waste to be substantial. Estimated chromium concentrations for sludges from processes using rutile and ilmenite ores are presented in Table 2 below, and indicate that elemental chromium concentrations in the treatment sludge are significant: approximately 12,000 ppm when rutile ore is the feed material, and approximately 500 ppm when ilmenite ore is used. These are derived figures, and the full basis for the derivation is set out in Appendix 1. The assumptions made for this derivation are as follows:

- The chromium oxide content of the feed ores are 0.15% for ilmenite ores, based on typical values (see p. 3 above).

Since significantly higher chromium concentrations have been reported (id.), this is believed to be a conservative assumption.

--Virtually all of the chromium in the ore will be removed during the process purification step. This assumption is somewhat aggressive, but is believed to be realistic, since the purification step is designed to remove heavy metal impurities, and moreover, available sampling data (1, as presented in Fig. 1) indicates all chromium being removed at this point in the process. Although small amounts of chromium may remain in the product, or are removed in the product washing step of the process, these amounts are believed to be insubstantial, and not of regulatory significance.

--All of the chromium present in the process wastewater (combined streams A and D in Fig. 1) will precipitate and will therefore be present in the wastewater treatment sludge. This assumption is also somewhat aggressive, since some traces of chromium may be discharged in the effluent. The overwhelming percentage, however, will not be so discharged (because of the relative insolubility of chromium hydroxide). Since elemental chromium is non-degradable, it will persist in the treatment sludge and in leachates therefrom.

Using these assumptions, chromium concentrations in the treatment sludge are derivable by first determining the respective total TiO_2 production from ilmenite and rutile ores, by determining the quantity of each ore required to generate this amount of product, determining the quantity of chromium oxide in this amount of ore and by converting this value into chromium (since virtually all chromium in the ore is assumed to be present in the wastewater treatment sludge).

Total potential waste loadings are quite substantial. It is estimated that rutile ores generate approximately 0.055 kkg of waste per kkg of product whereas ilmenite ores generate between 2.23 and 3.40 kkg of waste per kkg of product (1,7). As shown in Table 2, the total quantity of wastewater treatment sludge generated from this process is estimated to contain over 600 kkg of chromium. Another report (8) estimates the generation of 1.4 kkg chromium per 10^3 kkg of product resulting in a similar figure for total chromium in the waste.

D. Waste Management

Current practices in this industry for the management of this waste are as follows:(1)

- ° One plant disposes of the waste on-site in lined lagoons (with monitoring).
- ° One plant disposes of most of the waste by deep well injection (with monitoring).
- ° Two plants transport the waste off-site to a common unlined landfill (no monitoring).(7)

Table 2

QUANTITY OF WASTEWATER TREATMENT SLUDGE GENERATED BY THE TITANIUM DIOXIDE CHLORIDE
PROCESS AND CHROMIUM CONTENT OF THE WASTEWATER TREATMENT SLUDGE

State	Number of Plants	Capacity(1) kkg/yr	Ore Used	Sludges Generated (Dry basis)(7)		Total Chromium in Wastewater Treat- ment Sludge (Dry) (kkg/yr)
				(kkg/yr)(1)	Chromium in Sludge (dry basis)%*	
California	1	27,200	Rutile	1,500	1.23	18
Delaware	1	99,000	Ilmenite	337,000**	0.051	171
Georgia	1	36,400	Rutile	2,000	1.23	24
Maryland	1	26,300	Rutile	1,800	1.23	22
Mississippi	1	45,000	Rutile	2,500	1.23	30
Ohio	2	51,700	Rutile	9,700	1.23	116
Tennessee	1	<u>207,000</u>	Ilmenite	<u>461,000</u>	0.051	<u>235</u>
Totals	8	492,600		815,500		616

* See Appendix I for calculations.

** Of this quantity, up to 150,000 kkg per year is sold as FeCl_3 .

- ° One plant transports the waste off-site to an unlined landfill.
- ° Two plants combine the chloride process wastewater with that from titanium dioxide sulfate process operations. One plant neutralizes this combined wastewater prior to discharge and disposes of the solids in an on-site landfill. The other facility neutralizes only part of its wastewater and uses contractors to transport the formed solids off-site to a landfill.
- ° One plant sells a portion of its waste as ferric chloride (as much as 150,000 kkg per year) and disposes of the remainder by ocean barging.^{*/}

III. Discussion Basis for Listing

A. Hazards Posed by the Waste

As shown above, chromium may be present in this waste in substantial concentrations, from roughly 500-12,000 ppm. Chromium is present in the wastewater treatment sludge primarily as the trivalent species, principally the hydroxide and also as the chloride. Depending on the presence of other metal ions, and the acidity or alkalinity of the specific

^{*/}Under §261.6 (which applies to sludges which fail a characteristic, as well as to listed wastes) this reused hazardous waste is subject to the requirements of Subtitle C up to the point of actual reuse. (See also 45 Fed. Reg. at 33092-094 (May 19, 1980) for a more detailed explanation of the current regulatory regime for reused hazardous wastes).

environment, oxidation to higher valence states will occur. Thus, these wastes may, after storage or disposal, contain chromium generally in the most stable tri- and hexavalent states. Both forms of chromium are toxic, though hexavalent chromium is more toxic and is an animal carcinogen.^{*/}(9)⁻ Section III B of this document discusses more fully the health and ecological effects of chromium.

The chromium components of this waste are capable of migration, mobility and persistence. Neutralization of the TiO_2 wastewater stream results in the precipitation of chromium as the hydroxide. Chromium hydroxide has limited migratory potential due to its low solubility (see Water Related Environmental Fate of 129 Priority Pollutants, supra, Vol. 1, Ch. 10).

However, chromium was shown to be extractable from an electroplating wastewater treatment sludge (in which chromium is present in the hydroxide form). Chromium leached from waste samples subjected to the proposed extraction procedure in concentrations as high as 400 mg/l, demonstrating ability to migrate in relatively mild acidic environments. (see listing background document, "Electroplating and Metal Finishing Operations.")

^{*/}See EP Toxicity Background Document at pp. 109-112 summarizing data showing that trivalent chromium is likely to oxidize to the more dangerous hexavalent chromium upon environmental release, even in mild environmental conditions. Thus, exposure to hexavalent chromium is possible even if chromium migrates in the trivalent state. To the same effect, see Water-Related Environmental Fate of 129 Priority Pollutants, Vol. 1, U.S. EPA 1979, Ch. 10, at 10-3.

In addition, chromium was shown to be extractable from a neutralized spent pickle liquor sludge sample (in which chromium is present in the hydroxide form), in concentrations (429 ppm) sufficient to create substantial hazard (18) (see listing background document "Steel Finishing").^{*/}

Thus chromium, even when present as the relatively insoluble hydroxide, is capable of migrating from neutralized sludges. An acidic environment can reasonably be expected to occur in the waste management practices for titanium dioxide wastewater treatment sludges. Such an environment could result from inadequate neutralization of the acidic waste stream, from co-disposal of neutralized sludges with acidic wastes, or as a consequence of disposal in areas subject to rainfall. Seven of the eight TiO_2 facilities are located east of the Mississippi, in areas where rainfall is becoming more acidic.(4,5).

An additional consideration is the probable presence in the waste of chromium as the chloride. It is expected to be entrained by the precipitated chromium hydroxide, and may, in fact, be present in high concentration if the wastewater is not efficiently or adequately neutralized. Chromium chloride is extremely soluble (430,000 mg/l), and thus has very high migratory potential.(16)

*pH and test conditions unknown

Improper management of this wastewater treatment sludge may consequently result in ground- and surface water contamination. Sludges accumulate in the bottom of wastewater treatment lagoons and remain there until dredging and final disposal. Chromium could leach out and contaminate groundwater if lagoons are unlined or lack adequate leachate collection systems; moreover, as shown on p.11 supra, few facilities use liners or collection devices in managing this waste. In addition, migratory potential of the waste would increase under acidic conditions. The solubilities of the different species of chromium differ but in general increase with acidity.⁽³⁾ Thus, though chromium has the ability to migrate under mild conditions, its ability to do so increases significantly with a decrease in pH. Accordingly, if the wastewater -- which, as Figure 1 illustrates, contains significant concentrations of HCl -- is poorly neutralized, the soluble chromium constituents in the waste are likely to remain in solution or be entrained in the precipitated sludges, resulting in increased migratory potential of chromium ions.

There is also a danger of migration into and contamination of surface waters if lagoons are improperly designed or managed. Thus, inadequate flood control measures could result in washout or overflow of ponded wastes.

As previously stated, five of the eight facilities which produce titanium dioxide via the chloride process ultimately

dispose of their wastewater treatment sludges in off-site unlined landfills. This practice could also lead to the release of chromium from the waste and subsequent groundwater contamination. Rainfall percolating through unlined landfills may cause the chromium constituents to migrate from the matrix of the waste into the environment. This is especially likely in areas where acid rainfall is prevalent, since, as previously discussed, chromium is more soluble in acid environments. Seven of the eight plants manufacturing titanium dioxide are located east of the Mississippi, in area of the country where rainfall is becoming more acidic.^(4,5) If these unlined treatment or disposal facilities are located in areas with permeable soils, the potential for groundwater contamination would be even greater.

In addition to difficulties caused by improper site selection, uncontrolled landfills are not likely to have leachate control practices or surface run-off diversion systems that are sufficient to diminish or prevent leachate percolation through the soil underneath the site to groundwater. It should also be noted that two of the sites currently employ groundwater monitoring at existing on-site disposal facilities, which would indicate their concern for the management of these wastes (i.e., the fact that they may pose a hazard of groundwater contamination).

With regard to the fate of chromium, the heavy metal contaminant present in the waste is an element which persists

indefinitely in some form and therefore may contaminate drinking water sources for long periods of time.

The Agency has determined to list wastewater treatment sludge from the production of TiO_2 pigment using chromium bearing ores by the chloride process as a T hazardous waste, even though the waste may be evaluated by the E characteristic, and even though chromium concentrations in the EP extract from this waste from individual sites may not always be 100 times the national interim primary drinking water standard. The Agency believes that there are other factors in addition to the metal concentrations in a waste extract which justify the T listing. Some of these factors already have been identified, namely that chromium is believed to be present in the waste in high concentrations, that present industry disposal practices may sometimes be improper, that the location of most of the disposal sites are in areas of acid rainfall and so may increase the potential of chromium to leach from the waste, and that chromium will persist indefinitely in some form in the environment.

The quantity of the waste, is an additional supporting factor in the listing of this waste as hazardous. As indicated above, these wastewater treatment sludges are generated in large quantities (800,000 kkg/yr) and contain large amounts of the constituent of concern (>600 kkg). These large quantities of chromium pose the danger of large scale contamination of ground and surface water should mismanagement occur. Addi-

tionally, since these wastes are disposed of at relatively few disposal sites, the chance for environmental insult increases in these areas. For example, it is calculated that approximately 230 kkg of chromium will be disposed of annually at a single site. Further, should contamination occur, it will be for long periods of time, since chromium persists virtually indefinitely. 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 constituent in the waste, and, in the Agency's view, support a T listing.

B. Health and Ecological Effects of Chromium

The hexavalent forms of chromium are more toxic than the trivalent species. Although trivalent chromium is the predominant species in the waste sludges of concern in this document, conversion of an unknown extent to the hexavalent species is expected to occur.

Hexavalent chromium is an animal carcinogen,⁽⁹⁾ and there is some epidemiologic evidence that it may be a human carcinogen as well;⁽⁹⁾ EPA's Carcinogen Assessment Group has listed it as such. Bacterial mutagenic effects have been reported as well as cytogenetic effects in exposed workers using hexavalent chromium compounds.⁽¹¹⁾ Trivalent chromium has not shown to be either mutagenic or carcinogenic. A single study, of doubtful significance, reported teratogenic

effects of both forms of chromium to chick embryos.(9) Other chronic effects of chromium compounds occur at very high dose levels in some industrial situations.(11)

The acute toxic effects of trivalent chromium for fish are more pronounced in soft than in hard water.(10) Hexavalent chromium, at low concentrations, is toxic to many aquatic species. For the most sensitive aquatic species, Daphnia magna, a chronic no-effect level of less than 10 ug/l has been derived.(9) Hexavalent chromium (chromate) has been reported not to bioconcentrate in freshwater fish.(10)

EPA has estimated 800 ug/l as the concentration of hexavalent chromium in ambient water which will result in a 10^{-6} risk level of human cancer. The proposed freshwater standard for hexavalent chromium is 10 ug/l, not to exceed 110 ug/l. (12)

OSHA has established 1 mg/m^3 (8 hr TWA) as the workplace exposure limit in air for chromium metal and insoluble salts, and 0.5 mg/m^3 for soluble chromium compounds.(14) Additional information on the adverse health and environmental effects of chromium are described in Appendix A.

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APPENDIX I

ESTIMATE OF CHROMIUM CONCENTRATION IN WASTEWATER

TREATMENT SLUDGE FROM TiO_2 PRODUCTION (Chloride Process)

The amount of chromium in the wastewater treatment sludge is dependent upon the amount of chromium in the ore. The amount of chromium in both ilmenite and rutile ore is highly variable. In the United States, the chromium content of the ilmenite ores that are used ranges from less than 0.001% to 0.15% (1). Australian rutile ore, which is used domestically, contains about 0.19% chromium as the oxide (1). An estimate of the chromium content of the waste can be generated using these data, but it should be noted that plants can change ore source and thus their waste load. The following estimate is based upon a chrome oxide content of 0.15% for ilmenite ore and 0.19% for rutile ore. Chromium concentration in the treatment sludge can be estimated as follows:

1978 TiO_2 production = 615,853 kkg (*)

TiO_2 Chloride process capacity = 492,600 kkg (1)

TiO_2 Sulfate process capacity = 263,800 (1)

$$\begin{aligned} \text{Chloride process production} &= \frac{492,600}{492,600 + 263,800} \times 615,853 \text{ kkg} \\ &= 401,070 \text{ kkg } \text{TiO}_2 \end{aligned}$$

*Chemical and Engineering News, June 12, 1978, p.48.

From Tables 1 and 2:

$$\begin{array}{rcl} \text{ilmenite production} & - & \frac{306,000}{492,600} \times 401,070 \\ & = & 249,142 \text{ kkg TiO}_2 \end{array}$$

$$\begin{array}{rcl} \text{thus rutile production} & = & 401,070 \text{ kkg} - 249,142 \text{ kkg} \\ & = & 151,928 \text{ kkg TiO}_2 \end{array}$$

A. For ilmenite ore:

$$\begin{array}{rcl} \text{ore required}^{(3)} & - & \frac{1600 \text{ kkg ore}}{1000 \text{ kkg TiO}_2} \times 249,142 \text{ kkg TiO}_2 \\ & = & 398,627 \text{ kkg} \end{array}$$

$$\text{Cr}_2\text{O}_3 \text{ content} = 0.0015 \times 398,627 \text{ kkg ore} = 598 \text{ kkg}$$

$$\text{Cr content} = 598 \times 104/152 = 409 \text{ kkg Cr}$$

$$\text{Treatment sludge from ilmenite plants} = 798,000 \text{ kkg}^{(1)}$$

$$\begin{array}{rcl} \text{Cr concentration in sludges} & - & \frac{409 \times 100}{798,000} \\ & = & 0.051\% \end{array}$$

B. For rutile ore:

$$\begin{array}{rcl} \text{ore required}^{(7)} & - & \frac{1090 \text{ kkg ore}}{1000 \text{ kkg TiO}_2} \times 151,928 \text{ kkg TiO}_2 \\ & = & 165,600 \text{ kkg} \end{array}$$

$$\text{Cr}_2\text{O}_3 \text{ content} = 0.0019 \times 165,600 \text{ kkg ore} = 315 \text{ kkg}$$

$$\text{Cr content} = 315 \times 104/152 = 215 \text{ kkg}$$

Treatment sludges from rutile plants = 17,500 kkg

Cr concentrations in sludges = $\frac{215 \times 100}{17,500} = 1.23\%$

Paint Manufacturing

LISTING BACKGROUND DOCUMENT

PAINT MANUFACTURING

Solvent Cleaning Wastes from Equipment and Tank Cleaning (I,T)

Water and/or Caustic Cleaning Wastes from Equipment and Tank Cleaning (T)*

Wastewater Treatment Sludge (T)**

Emission Control Dust/Sludge (T)

I. SUMMARY OF BASIS FOR LISTING

The main source of hazardous wastes generated by the paint manufacturing industry is from the cleaning of mixing tanks and filling equipment. Floor and spill cleanup, cleanout of raw material supply tank cars and trucks, wastewater treatment and air pollution control are additional sources of hazardous waste.

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

*The spent caustic and its associated solids may also be corrosive due to the high pH of the caustic cleaning solution. At the present time, however, the Agency has insufficient data to substantiate listing this waste for this characteristic. Therefore, it will be the responsibility of individual manufacturers to determine whether the waste also exhibits this characteristic.

**In addition to being toxic, the wastewater treatment sludge may also be corrosive when caustic is used for tank cleaning and the caustic wash water (which may be corrosive) flows to the wastewater treatment plant. Since available data indicates that the sludge will be corrosive in only a few instances, the Agency is leaving it up to the individual generators to determine whether their waste also exhibits this characteristic.

appropriate management requirements under Subtitle C of

RCRA. This conclusion is based on the following considerations:

1. The four solid waste streams listed above are deemed toxic because each contains high concentrations of organic and/or inorganic contaminants. Specific contaminants contained in each waste may be summarized as follows:
 - ° Solvent cleaning wastes - lead and chromium
 - ° Water and/or caustic cleaning waste - lead, mercury, benzene, carbon tetrachloride, methylene chloride, tetrachloroethylene, naphthalene, di-(2-ethylhexyl)phthalate, di-n-butylphthalate and toluene.
 - ° Wastewater treatment sludges - chromium, lead, mercury, nickel, methylene chloride, and toluene.
 - ° Emission control dust/sludge - antimony, cadmium, chromium, lead, nickel, silver, cyanides, phenol, mercury, pentachlorophenol, vinyl chloride, 3,3-dichlorobenzidene, naphthalene, di(2-ethylhexyl) phthalate, di-N-butyl phthalate, benzene, toluene, carbon tetrachloride, methylene chloride and trichloroethylene.
2. In addition, solvent cleaning wastes are deemed hazardous because they consist of spent mineral spirits which are ignitable as defined by 40 CFR Part 261.21.
3. Present management of these wastes may be inadequate to prevent the toxic constituents in these wastes from migrating to groundwater and nearby surface waters.
4. The various physical forms of these wastes (e.g., liquid form, sludges, and dust of fine particulate composition) could allow the release of the hazardous constituents from their disposal environments. Exposure to an acidic environment could also encourage the solubilizing of the heavy metals

in the wastes (many plants are located in regions known to be subject to acid rainfall), subsequently increasing their concentrations in leachate. Many of the constituents of concern are also volatile and pose an inhalation hazard to persons coming in contact with the waste.

5. The transportation of these wastes to off-site facilities increases the possibility of exposure of these wastes to humans and the environment, should mismanagement occur.
6. Approximately 590,000 tons per year of hazardous wastes are generated by an estimated 1,500 paint manufacturing facilities. Such large quantities of wastes containing high concentrations of hazardous constituents increases the probability of damage to human health and the environment under improper disposal conditions.
7. These paint wastes have been mismanaged in the past, causing potential substantial hazard to human health and the environment.

II. INDUSTRY PROFILE AND MANUFACTURING PROCESS

Overall, the paint industry consists of an estimated 1,500 manufacturing plants. Table 1 presents an approximate breakdown of paint plants by state (1). Paint products manufactured at these sites fall into two general categories: solvent-thinned or water-thinned products. These products are also referred to as solvent-base or water-base formulations. Relatively few plants produce exclusively solvent-base or water-base paints (about 5.1 percent and 4.8 percent respectively). Common practice for paint plants is to manufacture both solvent and water-thinned products.

TABLE 1

GEOGRAPHICAL DISTRIBUTION OF PAINT PLANTS(1)

<u>EPA Region I</u>		<u>EPA Region II</u>		<u>EPA Region III</u>	
Connecticut	10	New Jersey	112	Delaware	3
Maine	3	New York	109	D.C.	0
Massachusetts	54	Puerto Rico	6	Maryland	20
New Hampshire	3	Virgin Islands	0	Pennsylvania	66
Rhode Island	5			Virginia	13
Vermont	<u>2</u>		<u> </u>	West Virginia	<u>4</u>
Total	77		227		106
<u>EPA Region IV</u>		<u>EPA Region V</u>		<u>EPA Region VI</u>	
Alabama	12	Illinois	106	Arkansas	7
Florida	69	Indiana	34	Louisiana	15
Georgia	35	Michigan	47	New Mexico	3
Kentucky	22	Minnesota	19	Oklahoma	9
Mississippi	5	Ohio	103	Texas	58
North Carolina	20	Wisconsin	34		
South Carolina	5				
Tennessee	<u>17</u>		<u> </u>		<u> </u>
Total	185		343		92

EPA Region VII

Iowa	13
Kansas	10
Missouri	51
Nebraska	2
	<hr/>
	76

EPA Region VIII

Colorado	11
Montana	3
North Dakota	0
Utah	4
Wyoming	1
	<hr/>
	20

EPA Region IX

Arizona	6
California	196
Hawaii	0
Nevada	1
	<hr/>
	203

EPA Region X

Alaska	1
Idaho	2
Oregon	20
Washington	<u>22</u>
Total	45

Figures 1 and 2 illustrate typical solvent-base and water-base paint manufacturing operations. Virtually all paint is made in batches. For solvent-base paints (see Figure 1), the mixing and grinding of raw materials (pigments, oils, solvents and resins) is accomplished in one production step. For high gloss paints, the pigments and a portion of the binder and vehicle are mixed into a paste of a specified consistency. This paste is fed to a grinder, which disperses the pigments by breaking down particle aggregates rather than by reducing the particle size. Two types of grinders are ordinarily used for this purpose: pebble or steel ball mills, or roll-type mills. Other paints are mixed and dispersed in a mixer using a saw-toothed dispersing blade, which is commonly referred to as a high speed disperser.

In the next stage of production, the paint is transferred to tinting and thinning tanks, occasionally by means of portable transfer tanks, but more commonly by gravity feed or pumping. Here, the remaining binder and liquid, as well as various additives and tinting colors, are incorporated. The finished product is then transferred to a filling operation where it is filtered, packaged and labeled.

Water-base paints are produced in a slightly different manner from solvent-base paints (see Figure 2). The pigments and extending agents are usually received in proper particle size, and the dispersion of the pigment, surfactant and binder into the vehicle is accomplished with a saw-toothed

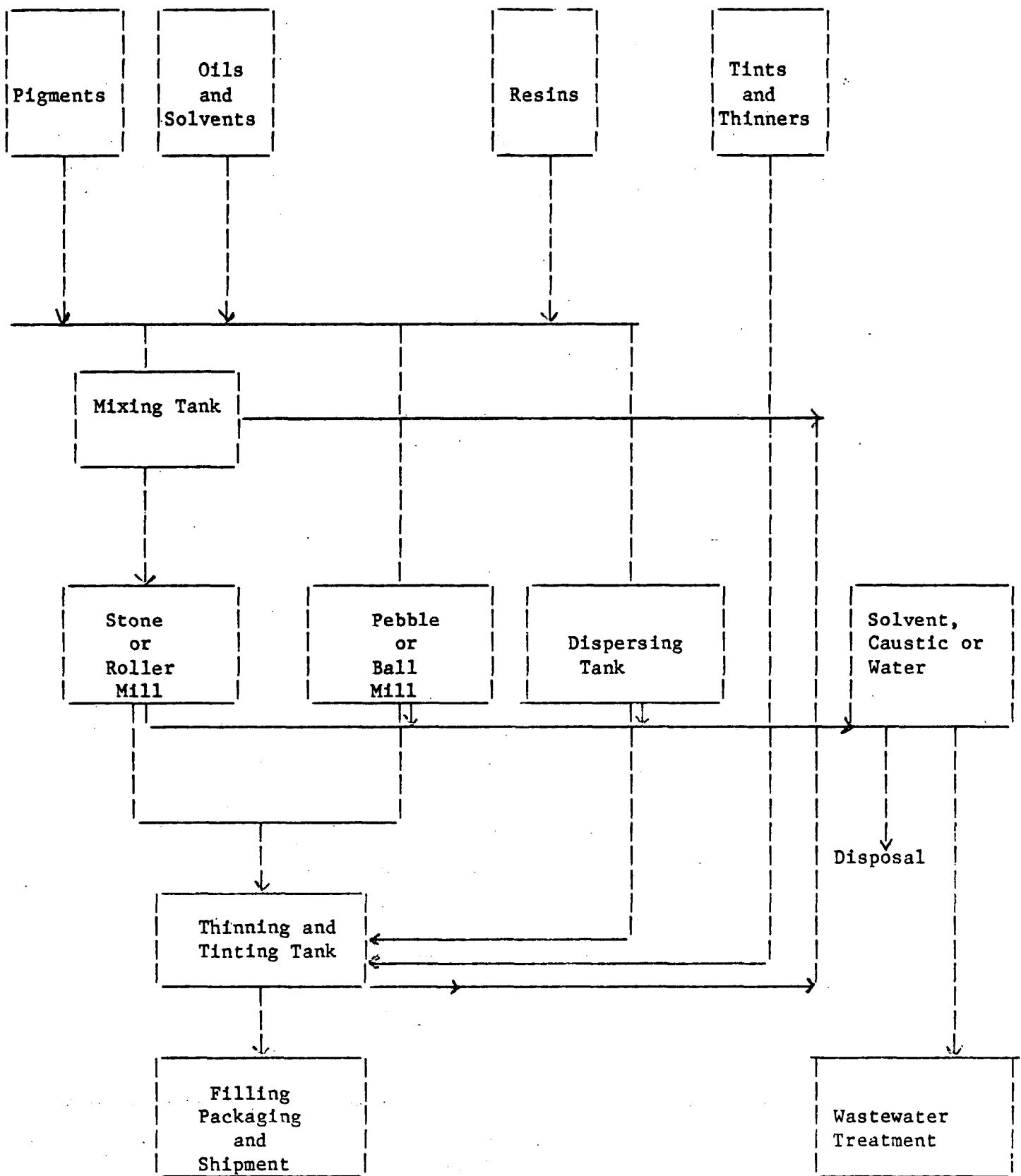


Figure 1 - Flow Diagram of Manufacturing Process for Solvent Base Paints

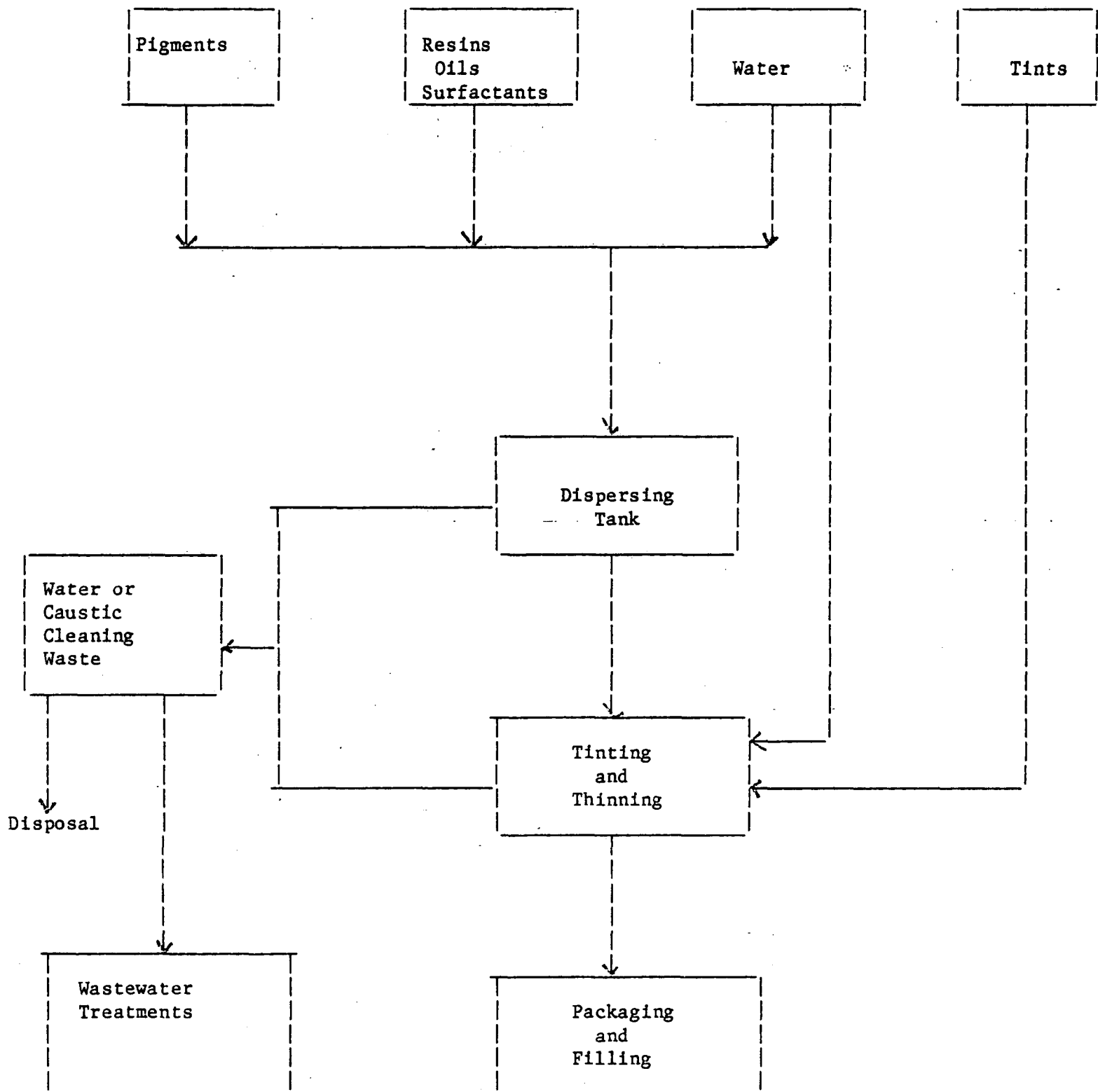


Figure 2 - Flow Diagram of Manufacturing Process for Water-Base Paints

high speed disperser. In small plants, the paint is thinned and tinted in the same tank, while in larger plants, the paint may be transferred to special tanks for the final thinning and tinting. Once the formulation is correct, the paint is transferred to a filling operation where it is filtered, packaged and labeled in the same manner as solvent-base paints.

III. GENERATION AND MANAGMENT OF LISTED WASTE STREAMS (1,2)

The four hazardous waste streams of concern are generated primarily as a result of the clean-up of tanks and other equipment. Table 2 summarizes the hazardous waste generation rates in the paint manufacturing industry.

Three specific methods of paint tank cleaning are commonly used in the Paint Industry. These cleaning methods include (1) solvent wash, (2) caustic wash and (3) water wash. Solvent wash is used exclusively for cleaning tanks used for solvent-based paint formulation. Caustic wash techniques may be used to clean solvent-base and water-base paint manufacturing tanks. Water washing techniques are also used in both the solvent-based and water-based segments of the Paint Industry. For solvent-base operations, water washing is usually used only to follow caustic washing of solvent-based tanks. For water-base operations, water washes often constitute the only tank cleaning operation. Periodic caustic cleaning of water-base paint tanks is also a common practice.

TABLE 2
HAZARDOUS WASTE GENERATION RATES
IN THE PAINT MANUFACTURING INDUSTRY (1,2)

<u>Waste</u>	<u>Tons Per Year</u>
Wastewater and Caustic Rinse Water	520,000(a)
Wastewater Treatment Sludge	39,200(b)
Solvent Cleaning Wastes (not reclaimed)	29,000
Air Pollution Control Residues	<u>1,700</u>
TOTAL	589,900

(a) Wash water and spent caustic that is disposed untreated as of June, 1980.

(b) Includes 42 plants that currently treat wash water and spent caustic generating 15 percent sludge, by volume.

1. Solvent Cleaning Wastes: Solvent-base paint mixing tanks and other accessory equipment are cleaned with either solvent (primarily mineral spirits), caustic or a combination of the two. The used solvent is normally handled in one of three ways: (1) used in the next compatible batch of product as part of the formulation; (2) collected and redistilled either by the plant or an outside company; or (3) reused with or without settling until it loses its cleaning ability, or is "spent". When spent, the waste solvent is drummed and removed for disposal. If solids are settled out of the used solvent, the resultant sludge is also drummed and removed for disposal. The category "solvent cleaning wastes" thus includes both spent solvent and solids contained in the spent solvent. Sometimes the two are disposed of separately--i.e. the solids are settled out of the spent solvent and disposed of as a sludge, in which case both are deemed hazardous.

Approximately 29,000 tons of solvent cleaning wastes (not reclaimed) are generated per year.(2)

2. Water and/or Caustic Cleaning Wastes: Tanks and equipment used to manufacture water-based paint are generally washed with water. Rinse water is usually handled in one of four ways: (1) used in the next compatible batch of paint as part of the formulation; (2) discharged with or without treatment as wastewater; (3) removed for off-site disposal; or (4) reused either with or without treatment

to clean tanks and equipment until spent. If sludge is settled out of the spent rinse water, it is disposed of as a solid waste.

Caustic (NaOH) is used to clean tanks and equipment used in the manufacture of both solvent and water based paints. Most plants using caustic reuse the solution until it loses some of its cleaning ability. At that time, it is disposed of as either a solid waste or wastewater with or without neutralization of other treatment. Following caustic cleaning, tanks and equipment are usually rinsed with water. This wastewater is handled in one of three ways: (1) recycled to the caustic solution as make-up water; (2) drummed for disposal as a solid waste; (3) discharged as wastewater with or without pretreatment--sometimes first combined with other plant wastewater prior to treatment or disposal. Caustic cleaning techniques can also create a sludge when a recirculating caustic system is employed. The sludge is comprised of paint solids which often accumulate at the bottom of the caustic reservoir and must periodically be removed when caustic make-up is required.

The category "water and/or caustic cleaning wastes" thus includes spent rinse water, spent caustic, and any solids associated with wastes generated by water cleaning and caustic cleaning of equipment and tanks. Sometimes the two phases are disposed of separately--the solids are settled out of the spent rinse water and/or caustic

wash and disposed of as sludges, in which case both phases are included in this listing. Approximately 520,000 tons per year of wastewater and caustic rinse water are currently generated per year.

3. Wastewater Treatment Sludges are generated by the paint industry primarily by the physical/chemical treatment of equipment and tank rinsewater, caustic cleaning waste, and other miscellaneous wastewater streams generated at various parts of the plant.

The sludge produced from wastewater treatment is generally 15 percent by volume of the plant wastewater quantity (1). Proposed pretreatment standards may eliminate the generation of these wastewater treatment sludges (1). Instead, 20% of the wastewater generated may be hauled to disposal sites. This could result in up to 156,000 tons of wastewater being hauled to disposal sites annually.

4. Emission Control Dust/Sludge: Air pollution control devices are usually applied to plant ventilation exhausts to prevent outside air contamination. The purpose of in-plant ventilation is to remove airborne dusts and solvent fumes that pose either a health hazard to workers or create an explosive atmosphere. The residues from the control dusts consist of dust and particulate matter collected in filter systems which are usually associated with emptying bags into process mixers (2). Some plants

use a wet emission control system, in which case a sludge (rather than dust) is generated. (Small plants do not normally employ emission control equipment.(2)) Approximately 1,700 tons of air pollution control residues are generated per year.(2)

Disposal Practices

Treated and untreated wastewaters (water and/or caustic cleaning wastes) are discharged to POTWs or placed in drums for disposal in landfills.(1) About 19.7 percent of all paint plants engage contract haulers to remove paint wastewater.(1) Table 3 summarizes the major wastewater disposal methods used in the paint industry. As shown by the table, discharge to POTWs is the most frequently used disposal method.

The 29,000 tons per year of unreclaimed solvent are disposed primarily in landfills(2) in 55-gallon drums. Still bottoms from solvent reclaiming operations are also sealed in drums and disposed of in landfills.(1)

Sludges generated during physical/chemical wastewater treatment processes are disposed of in one of two general ways--by contract hauling and by landfill. At least one large paint producer stores paint wastewater treatment sludge in an on-site impoundment.(1) Most contract haulers dispose of the sludge in landfills, although a small number incinerate or reclaim it (1). Approximately 19% of all paint plants do not know what the contract hauler does with the waste.(1)

Emission control dusts/sludges are generally disposed of by contract hauling.(2)

IV. HAZARDOUS PROPERTIES OF THE WASTE

A. Waste Composition

In general, the EPA has designated the wastes generated by water and/or caustic or solvent rinsing of paint manufacturing equipment as hazardous wastes because they are contaminated with toxic chemicals found in paint. The products and raw materials of the paint industry have been shown to contain at least 21 organic and inorganic priority pollutants(1) (see Table 4). Since the purpose of these cleaning operations is to remove unusable paint product, these contaminants necessarily will be found in the various cleaning wastes. The sludges resulting from settling of these wastes are also expected to contain some of these toxic constituents, as are the wastewater treatment sludges and air pollution control dusts/sludges. The specific constituents and hazards associated with each listed waste are described in greater detail below. The health and environmental hazards associated with the specific constituents in the listed wastes are described on pp. 33-57 and in Appendix A.

TABLE 3
WASTEWATER DISPOSAL METHODS (1)

<u>Disposal Method</u>	<u>All Plants</u>	
	<u>Number of Plants*</u>	<u>Percent of Total</u>
Complete Reuse	88	6.4
Partial Reuse	262	19.1
Evaporation	125	9.1
Discharge to City Sewer	475	34.6
Discharge to Storm Sewer	68	4.9
Discharge to Receiving Stream	13	0.9
Impoundment on Plant Property	87	6.3
Incineration	5	0.4
Contract Hauling	271	19.7
Landfilled	107	7.8
Well or Septic Tank	13	0.9
Spray Irrigation	8	0.6

*Some plants indicated multiple disposal methods.

TABLE 4

TOXIC CONSTITUENTS IN RAW MATERIALS
USED BY THE PAINT INDUSTRY⁽¹⁾

Responders Indicating Usage of Raw Materials Containing
Specific Priority Pollutants*

Priority Pollutant	Minimum		Maximum	
	No. of plants	Percent	No. of Plants	Percent
Antimony	166	12.1	243	17.7
Cadmium	260	18.9	312	22.7
Chromium	1042	75.8	1083	78.8
Lead	833	60.6	1016	73.9
Nickel	156	11.4	395	28.7
Silver	250	18.2	440	32.0
Cyanides	860	62.6	1064	77.4
Phenol	665	48.4	765	55.7
Mercury	627	45.6	627	45.6
Pentachlorophenol	190	13.8	190	13.8
Vinyl Chloride	550	40.0	563	41.0
3,3-Dichlorobenzidene	409	29.8	412	30.0
Naphthalene	772	61.6	772	56.2
Di-(2 Ethylhexyl)Phthalate	338	24.6	338	24.6
Di-N-Butyl Phthalate	354	25.8	354	25.8
Benzene	66	4.8	66	4.8
Toluene	961	69.9	998	72.6
Carbon Tetrachloride	8	0.6	8	0.6
1,1,1 Trichloroethane	140	10.2	140	10.2
Methylene Chloride	305	22.2	305	22.2
Trichloroethylene	77	5.6	77	5.6

(*) Data generated from 1374 responses to paint industry "308" survey. Since many of the raw materials included in the 308 Data Collection Portfolio can contain more than one toxic pollutant, the Agency was unable to obtain unambiguous counts for the occurrence of particular toxic pollutants. A conservative approach was taken because of this. When the Data Collection Portfolio response did not indicate clearly which toxic pollutant was in use, the Agency made two counts - one including neither, one including both. This gave a maximum and minimum count for toxic pollutants.

Solvent Cleaning Wastes

Solvent cleaning wastes are considered hazardous because they have been documented to contain significant concentrations the two toxic heavy metals lead and chromium. In addition to posing a toxicity hazard, the solvent cleaning waste is also considered hazardous because the solvents employed in the cleaning process, primarily mineral spirits, are ignitable. The flash point of mineral spirits is 104°F (4) and therefore meets the §261.21 characteristic of ignitability (i.e. <140°F for liquids). The following data from state manifests illustrates both the significant heavy metal concentrations in these wastes, and the fact that the wastes' flashpoint meets the criteria for ignitability (5,6):

1. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

Waste Name: Still bottoms and thinner sludge

Quantity: 120,000 gallons (liquid)

Percent Analysis: 68.2% Solvents

31.8% Pigments and Resins

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>
	Cr	27.6
	Pb	112.9

Flashpoint: 70°F

2. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

Waste Name: Paint Sludges

Quantity: 458,000 gallons

Percent Analysis: 53% Solvents

45% Pigment and Binder

2% Inorganic Residue

Flashpoint: 110°F

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Total Concentration (ppm)</u>
	Cr	166
	Pb	1203

3. State: New Jersey

Source: Industrial Waste Surveys, New Jersey Department
of Environmental Conservation

Waste Name: Dirty Wash Solvent

Quantity: 37,000 gallons/year (liquid)

Percent Analysis: 85% Solvents

10% Resins

5% Pigments

<u>Chemical Analysis:</u>	<u>Contaminant</u>	<u>Total Concentrations (ppm)</u>
	Chromates	7000
	Lead	3000

Waste Properties: Flammable, Toxic (reported by generator)

In summary, solvent cleaning wastes are being listed as hazardous because (1) the solvents used to clean tanks and equipment are ignitable; and (2) the solvent cleaning wastes have been documented as containing the toxic compounds lead and chromium, in significant concentrations.

Water and/or Caustic Cleaning Wastes

The Administrator has classified water and/or caustic cleaning wastes as hazardous because of the levels of ten toxic constituents found in samples of the waste. Table 6 summarizes data which substantiate EPA's listing of these wastes as hazardous. These data were selected from EPA's Development Document for Effluent Limitations Guidelines and Standards for the Paint Formulating Point Source Category.⁽¹⁾ (Note that "untreated wastewater" samples are representative of water and/or caustic cleaning wastes before treatment.) These data indicate that lead, mercury, benzene, carbon tetrachloride, methylene chloride, tetrachloroethylene, naphthalene, di(2-ethylhexyl) phthalate (DEHP), di-n-butylphthalate and toluene are typically found in water and/or caustic cleaning wastes. Concentrations of these toxic pollutants in the wastewaters exceed 10 or even 100 times the existing drinking water or ambient water quality standards.

Wastewater Treatment Sludge

The Administrator has classified wastewater treatment sludges from paint manufacturing as hazardous because of the levels of six toxic constituents found in samples of the waste. EPA tested samples of this waste from several plants and found that it contained inorganic and organic priority pollutants.⁽¹⁾ The data shown in Table 7 from EPA's Development for Effluent Limitations Guidelines and Standards for the Paint Formulating Point Source Category

TABLE 6
UNTREATED WASTEWATER* DATA -- SELECTED POLLUTANTS
1977/1978 SAMPLING PROGRAM (1)

HAZARDOUS CONSTITUENT	--- SAMPLES ANALYZED	NUMBER OF --- TIMES ABOVE DET. LIMIT	AVERAGE (mg/l)	MEDIAN (mg/l)	MINIMUM (mg/l)	MAXIMUM (mg/l)	MASS LOADING (KG/YEAR)**
Lead	60	45	6.300	.805	.022	80.000	4,475
Mercury	55	44	5.161	.500	.001	62.000	3,650
Benzene	31	18	1.933	.370	.020	9.900	800
Carbon tetrachloride	31	7	3.770	.014	<.010	30.000	675
Methylene chloride	31	17	31.878	.620	<.010	210.000	13,100
Tetrachloroethylene	31	16	.567	.175	<.010	4.900	232.5
Naphthalene	31	8	2.950	.054	<.010	18.000	600
Di (2-Ethylhexyl) Phthalate	31	9	.418	.140	<.010	2.810	105
Di-N-Butyl-Phthalate	31	13	5.745	.160	<.010	69.000	2,475
Toluene	31	27	17.966	2.500	.073	259.700	11,075

* Representative of water and/or caustic cleaning wastes before treatment.

**Assumes production 250 days per year.

TABLE 7

WASTEWATER TREATMENT SLUDGE DATA SUMMARY

1977/1978 SAMPLING PROGRAM (1)

HAZARDOUS CONSTITUENT	-----Number of----- SAMPLES TIMES ABOVE ANALYZED DET. LIMIT	AVERAGE (MG/L)	MEDIAN (MG/L)	MINIMUM (MG/L)	MAXIMUM (MG/L)	MASS LOADING (KG/YEAR)*
Chromium	39 37	7.050	.700	<.50	90.000	767.5
Lead	39 37	10.770	3.000	<.100	80.000	1065
Mercury	36 31	15.061	.640	.005	220.000	1687.5
Nickel	39 27	10.443	.200	.020	200.000	1132.5
Methylene chloride	9 8	120.201	1.735	.300	900.000	12,764.25
Toluene	9 8	44.740	.905	.130	350.00	4650

*Assumes production 250 days/year

indicate that chromium, lead, mercury, nickel, methylene chloride and toluene, are typically found in wastewater treatment sludge from paint manufacturing.

In addition to the EPA data, the following data from Illinois and New Jersey(5,6) indicate that wastewater treatment sludge from paint manufacturing contains elevated levels of chromium in both cases, and lead in one case. Further, an acid leaching test performed on one of the samples indicates that the chromium and lead can, in fact, be extracted at levels which exceed 10 and 100 times (respectively) the drinking water standards for these metals.(5,6)

1. State: Illinois

Source: Special Waste Disposal Applications, Illinois EPA

Waste Name: Paint Sludge

Quantity: 50,000 gallons

Percent Analysis: 50% Resins

45% Pigments

<1% Xylol, toluol, isopropyl alcohol

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Concentration in Waste (ppm)</u>	<u>Concentrations in Leachate (ppm)</u>
	Cr ⁺⁶	1500	1.3
	Pb	9200	5.4

2. State: New Jersey

Source: Industrial Waste Surveys, New Jersey Department of
Environmental Protection

Waste Name: Emulsion Paint Sludge

Quantity: 70,000 gallons/year (sludge)

Percent Analysis: 60% Water

20% TiO₂

20% Latex Solids

<u>Chemical Analysis:</u>	<u>Metal</u>	<u>Concentration in Waste (ppm)</u>
	Pb	300

Waste Properties: Irritant, toxic (reported by generator)

Emission Control Dusts/Sludges

The Administrator has classified emission control dusts/sludges as hazardous because the Agency has reason to believe that these wastes contain substantial quantities of the toxic raw materials used in the formulation of paint products (see Section III, Generation and Management of Listed Waste Streams), and therefore that the wastes pose a substantial threat to human health and the environment. Specifically, this waste is being listed as a hazardous waste because of the presence of the following toxic constituents which are constituents of raw materials used in paint manufacturing:

antimony
cadmium
chromium
lead
nickel
silver
cyanides
phenol
mercury
pentachlorophenol
vinyl chloride
3,3'-dichlorobenzidene
naphthalene
di(2-ethylhexyl) phthalate
di-N-Butyl phthalate
benzene
toluene
carbon tetrachloride
1,1,1-trichloroethane
methylene chloride
trichloroethylene

If emission control residues are collected wet, scrubber water is often diverted to the wastewater treatment plant for treatment before disposal. In this case, the scrubber water becomes a source of the wastewater treatment sludge, which has already been demonstrated as being hazardous.

B. Potential for Substantial Hazard from Improper Waste Management

As shown above, these wastes contain a wide range of toxic organic and inorganic constituents, in many cases in significant concentrations. Many of these constituents, namely benzene, hexavalent chromium, carbon tetrachloride, tetrachloroethylene, 3,3'-Dichlorobenzidine, and trichloroethylene have been identified by the Agency's Carcinogen

Assessment Group as possessing substantial evidence of carcinogenicity, increasing Agency concerns as to the potential of these wastes to cause substantial harm if mismanaged. Under these circumstances, the Agency requires assurance that waste constituents will not migrate and persist should mismanagement occur.

Such assurance does not appear possible here since most waste constituents appear quite capable of migration in substantial concentrations, and of mobility and persistence upon environmental release. As shown in Table 8, most of the organic compounds in these wastes are very water soluble, and some (such as phenol) extremely so. The heavy metals are likewise known to be capable of migrations in leachate. These compounds thus present a danger of migration via a groundwater pathway if exposed to a leaching medium.

Other compounds, particularly benzene, vinyl chloride, toluene, trichloroethylene, 1,1,1'-trichloroethane, and methylene chloride, are significantly volatile and could pose an inhalation hazard to environmental receptors in the vicinity of improperly disposed wastes.

These constituents are likewise capable of mobility and persistence upon environmental release. Many constituents have in fact been involved in damage incidents resulting from improper waste management, empirically demonstrating mobility and persistence of waste constituents. For example,

Table 8*

Compound	Vapor Pressure (mm Hg)	Solubility in Water
Antimony	Varies, depending on which salt of of the metal is present in the waste.	
Cadmium		
Chromium		
Lead		
Nickel		
Silver		
Cyanides		
Mercury		
Phenol	0.2mm at 20°C ⁸	82 g/l at 15°C ⁸
Pentachlorophenol	.00011mm at 20°C ⁸	14 mg/l at 20°C ⁸
Vinyl Chloride	2,660mm at 25°C ⁸	1.100 mg/l at 25°C ⁸
3,3'-Dichlorobenzidene	low	4 mg/l ¹¹
Naphthalene	1mm at 53°C ⁸	30 mg/l ⁸
Di-2-Ethylhexylphthalate	1.2mm at 200°C ⁸	50 mg/l ⁹
Di-n-Butylphthalate	0.1mm at 115°C ⁸	400 mg/l at 28°C ⁸
Toluene	28.4 at 25°C ⁸	470 mg/l at 25°C ⁸
Benzene	76mm at 20°C ⁸	1,780 mg/l at 20°C ⁸
Trichloroethylene	77 at 25°C ⁷	1,000 mg/l at 20°C ⁷
1,1,1-trichloroethane	100 at 20°C	950 mg/l at 25°C
Methylene Chloride	350 at 20°C	20,000 mg/l at 25°C ⁷
Tetrachloroethylene	19 at 25°C ⁷	150 mg/l at 25°C ⁷

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

trichloroethylene, benzene, vinyl chloride, methylene chloride, and tetrachloroethylene were all involved in the contamination of drinking water sources in New Hanover, North Carolina. (Muskie report) Toluene and benzene are among the constituents present in water and air samples taken in the Love Canal area. ("Love Canal Public Health Bomb", a Special Report to the Governor and Legislature, New State Department of Health (1978)). Trichloroethylene and phenol were involved in a damage incident in Sehigh Co., Pa. where industrial wastes contaminated drinking water wells. (Muskie) Heavy metals and cyanides likewise have been involved in numerous damage incidents from improper waste disposal. (Muskie) Pentachlorophenol has been detected in surface water and finished drinking water (Appendix B), and is only moderately degradable. (Id.)

The remaining compounds likewise appear capable of mobility and persistence. The two phthalate esters present are mobile (particularly in soils low in organic content), and are capable of persistence in most environments, although subject to biodegradation. Both esters are also bioaccumulative, so that exposure to small concentrations may still prove dangerous. (11)

3,4-dichlorobenzidine has limited mobility in clay, or in soils high in organic content (11), but could be mobile in other media. Photolysis is the most significant degradation mechanism (11), and so would not effect this compound's persistence in groundwater.

Napthalene is likewise capable of migration through soils (11), and since it is not subject to hydrolysis (although it is biodegradable) (11), could persist in the abiotic conditions of most aquifers. These constituents thus have the capacity for migration, mobility and persistence, raising the possibility of potential hazard if the wastes are mismanaged.

Additionally, present management and disposal practices (see Section III) for these hazardous wastes may be inadequate to protect human health and the environment from exposure to the toxic constituents shown to be present in the wastes. Landfilling of any of the listed wastes in unsecure landfills could contaminate underlying groundwater or nearby surface water as the waste releases toxic constituents.

In particular, landfilling of liquid wastes such as the water and/or caustic cleaning waste, solvent cleaning waste, or a sludge which has not been dewatered, may pose a threat to water supplies because many of the toxic constituents present in the liquid waste are already solubilized in the liquid and would tend to pass more quickly through a landfill, even without the percolating action of rainwater on the landfill. The state manifest information presented above indicates that some of these toxic constituents will indeed be released from the waste. These wastes thus could contaminate drinking water supplies and pose a threat to human health and the environment through ingestion of water contaminated with the toxic constituents of concern.

Dewatered sludges--wastewater treatment sludges or air pollution (emission) control sludges--also pose a threat to human health and the environment if mismanaged. Extraction data have shown that the wastewater treatment sludges sometimes leach contaminants in excess of ten times the drinking water standard for chromium and lead. These data indicate that the sludges contain chromium and lead in a soluble form and thus could be released in harmful concentrations.

In general, if these wastes should be exposed to an acid environment, for example, disposed in landfills containing organic refuse or disposed in areas subject to acid rainfall, these constituents' concentrations in leachate would be similar to concentrations shown by the leaching data from the state manifests. As indicated in Table 1, many of these plants are located in regions known to be subject to acid rainfall (east of the Mississippi).

The dry air pollution (emission) control residue could pose an additional hazard. These emission control dusts are of a fine particulate composition, and therefore a large surface area is exposed to leaching action of any percolating medium. Dusts can pose a hazard in addition to that of ground and surface water contamination. Airborne exposure to, for instance, lead and chromium compounds escaping from air pollution control dusts poses an inhalation

hazard. These minute particles could be dispersed by the 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 particles would be jeopardized.

A further consideration in the regulation of these hazardous wastes is that they are transported to off-site disposal facilities. This increases the likelihood of their being mismanaged, i.e., uncontrolled transportation may result either in their not being properly handled during transport or their not reaching their destination at all. A transportation and manifest system combined with designated standards for the management of these wastes will greatly reduce their availability to harm to humans and the environment. In fact, many generators of these wastes actually indicated that at the present time they are ignorant of the ultimate disposition of the wastes they give to contract haulers (see pp. 14-15 above). In fact, in a recent damage incident, a number of 55 gallon drums of paint sludge were haphazardly dumped on a house farm north of Richmond, Virginia. These drums were traced back to a Maryland paint company. (Washington Post, June 23, 1980, at B 1.) The danger of improper transport of these wastes thus appears very high.

These wastes are generated in very substantial quantities (See Table 2) and contain significant concentrations of the

toxic constituents of concern (see previously sited data). Large amounts of these contaminants pose the danger of polluting large areas of ground and surface waters near an unsecure landfill. Contamination could also occur for any long periods of time, since large amounts of pollutants are available for environmental loading. Attenuative capacity of the environment surrounding an inadequate 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 the harmful constituents in the wastes.

V. Health and Environmental Effects (10)

The following contaminants of paint wastes are designated as priority pollutants under Section 307(a) of the Clean Water Act:

- antimony
- cadmium
- chromium
- lead
- mercury
- nickel
- silver
- cyanides
- phenol
- pentachlorophenol
- vinyl chloride
- 3,3-dichlorobenzidene
- benzene
- carbon tetrachloride
- methylene chloride
- tetrachloroethylene
- naphthalene
- di (2-ethylhexyl) phthalate
- di-N-butyl-phthalate
- toluene
- trichloroethylene

Lead is also regulated under the Clean Air Act. Proposed or final standards have been issued for most of these chemicals under the Occupational Safety and Health Act of 1970. More specific information on the health effects of these chemicals are summarized below. For further information on the health effects of all of these constituents, see Appendix A.

Antimony

Essentially no information on antimony-induced human health effects has been derived from community epidemiology studies. The available data are in literature relating effects observed with therapeutic or medicinal uses of antimony compounds and industrial exposure studies. Large therapeutic doses of antimonial compounds, usually used to treat schistosomiasis, have caused severe nausea, vomiting, convulsions, irregular heart action, liver damage, and skin rashes. Studies of acute industrial antimony poisoning have revealed loss of appetite, diarrhea, headache, and dizziness in addition to the symptoms found in studies of therapeutic doses of antimony.

For the protection of human health from toxic properties of antimony ingested through water and through contaminated aquatic organisms, the ambient water criterion is determined to be 0.145 mg/l.

Antimony compounds remaining in wastewater treatment sludge under anaerobic conditions may be connected to stibine (SbH_3), a very soluble and very toxic compound. Antimony is not known to be essential to the growth of plants, and has been reported to be moderately toxic. Therefore, sludge containing large amounts of antimony could be detrimental to plants if it is applied in large amounts to cropland.

Cadmium

Cadmium is an extremely dangerous cumulative toxicant (the metal is not excreted), causing progressive chronic poisoning in mammals, fish, and probably other organisms.

Toxic effects of cadmium on man have been reported from throughout the world. Cadmium may be a factor in the development of such human pathological conditions as kidney disease, testicular tumors, hypertension, arteriosclerosis, growth inhibition, chronic disease of old age, and cancer. Cadmium is normally ingested by humans through food and water as well as by breathing air contaminated by cadmium dust. Cadmium is cumulative in the liver, kidney, pancreas, and thyroid of humans and other animals. A severe bone and kidney syndrome known as itai-itai disease has been documented in Japan as caused by cadmium ingestion via drinking water and contaminated irrigation water. Ingestion of as little as 0.6 mg/day has produced this disease. Cadmium acts syn-

ergistically with other metals. Copper and zinc substantially increase its toxicity.

Cadmium is concentrated by marine organisms, particularly molluscs, which accumulate cadmium in calcareous tissues and in the visera. A concentration factor of 1,000 for cadmium in fish muscle has been reported, as have concentration factors of 3000 in marine plants and up to 29,600 in certain marine animals. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, and crustaceans appear to be more sensitive than fish eggs and larvae.

For the protection of human health from the toxic properties of cadmium ingested through water and through contaminated aquatic organisms, the ambient water criterion is determined to be 0.010 mg/l.

Data show that cadmium can be incorporated into crops, including vegetables and grains, from contaminated soils. Two Federal agencies have already recognized the potential adverse human health effects posed by the use of sludge on cropland. The FDA recommends that sludge containing over 30 mg/kg of cadmium should not be used on agricultural land. Sewage sludge contains 3 to 300 mg/kg (dry basis) of cadmium; mean = 10 mg/kg; median = 16 mg/kg. The USDA also recommends placing limits on the total cadmium from sludge that may be applied to land.

Chromium

The two chromium forms most frequently found in industry wastewaters are hexavalent and trivalent chromium. Some of it is reduced to trivalent chromium as part of the process reaction. The raw wastewater containing both valence states is usually treated first to reduce remaining hexavalent to trivalent chromium, and second to precipitate the trivalent form as the hydroxide. The hexavalent form is not removed by lime treatment.

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled, and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Hexavalent chromium has been identified by the Agency's Carcinogen Assessment Group as exhibiting substantial evidence of being carcinogenic. Levels of chromate ions that show no effect in man appear to be so low as to prohibit determination, to date.

The toxicity of chromium salts to fish and other aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially the effect of water hardness. Studies have shown that trivalent chromium is more toxic to fish of some types than is hexavalent chromium. Hexavalent chromium retards growth of one fish species at 0.0002 mg/l. Fish food organisms and other lower forms of aquatic life are extremely

sensitive to chromium. Therefore, both hexavalent and trivalent chromium must be considered harmful to particular fish or organisms.

For the protection of human health from the toxic properties of chromium (except hexavalent chromium) ingested through water and contaminated aquatic organisms, the recommended water quality criterion is 0.050 mg/l. For the maximum protection of human health from the potential carcinogenic effects of exposure to hexavalent chromium through ingestion of water and contaminated aquatic organisms, the ambient water concentration is zero.

Chromium is not destroyed when treated by wastewater treatment (although the oxidation state may change), and will either pass through to the wastewater treatment effluent or be incorporated into the wastewater treatment sludge. Both oxidation states can cause wastewater treatment inhibition and can also limit the usefulness of municipal sludge.

Chromium not passed through a wastewater treatment plant will be retained in the sludge, where it is likely to build up in concentration. Disposal of sludges containing very high concentrations of trivalent chromium can potentially cause problems in secure landfills. Incineration, or similar destructive oxidation processes can produce hexavalent chromium from lower valence states. Hexavalent chromium is potentially more toxic than trivalent chromium. In cases where high rates of chrome sludge application on land are used, distinct growth inhibition and plant tissue uptake have been noted.

Lead

Lead ingested by humans produces a variety of toxic effects including impaired reproduction ability, disturbances in blood chemistry, neurological disorders, kidney damage, and adverse cardiovascular effects. Exposure to lead in the diet results in permanent increase in lead levels in the body. Most of the lead entering the body eventually becomes localized in the bones where it accumulates. Lead is a carcinogen or cocarcinogen in some species of experimental animals. Lead is teratogenic in experimental animals. Mutagenicity data are not available for lead.

For the protection of human health from the toxic properties of lead ingested through water and through contaminated aquatic organisms the ambient water criterion is 0.050 mg/l.

Mercury

Mercury can be introduced into the body through the skin and the respiratory system as the elemental vapor. Mercuric salts are highly toxic to humans and can be absorbed through the gastrointestinal tract. Fatal doses can vary from 1 to 30 grams. Chronic toxicity of methyl mercury is evidenced primarily by neurological symptoms. Some mercuric salts cause death by kidney failure.

Mercuric salts are extremely toxic to fish and other aquatic life. Mercuric chloride is more lethal than copper, hexavalent chromium, zinc, nickel and lead towards fish and aquatic life. In the food cycle, algae containing mercury up

to 100 times the concentration in the surrounding sea water are eaten by fish which further concentrate the mercury. Predators that eat the fish in turn concentrate the mercury even further.

For the protection of human health from the toxic properties of mercury ingested through water and through contaminated aquatic organisms the ambient water criterion is determined to be 0.0002 mg/l.

In sludges, mercury content may be high if industrial sources of mercury contamination are present. Little is known about the form in which mercury occurs in sludge. Mercury may undergo biological methylation in sediments, but no methylation has been observed in soils, mud, or sewage sludge.

The mercury content of soils not receiving additions of POTW sewage sludge lie in the range from 0.01 to 0.5 mg/kg. In soils receiving POTW sludges for protracted periods, the concentration of mercury has been observed to approach 1.0 mg/kg. In the soil, mercury enters into reactions with the exchange complex of clay and organic fractions, forming both ionic and covalent bonds. Chemical and microbiological degradation of mercurials can take place side by side in the soil, and the products - ionic or molecular - are retained by organic matter and clay or may be volatilized if gaseous. Because of the high affinity between mercury and the solid soil surfaces, mercury persists in the upper layer of soil.

Mercury can enter plants through the roots, it can readily move to other parts of the plant, and it has been reported to

cause injury to plants. In many plants mercury concentrations range from 0.01 to 0.20 mg/kg, but when plants are supplied with high levels of mercury, these concentrations can exceed 0.5 mg/kg. Bioconcentration occurs in animals ingesting mercury in food.

Nickel

The toxicity of nickel to man is thought to be very low, and systemic poisoning of human beings by nickel or nickel salts is almost unknown. In non-human mammals nickel acts to inhibit insulin release, depress growth, and reduce cholesterol. A high incidence of cancer of the lung and nose has been reported in humans engaged in the refining of nickel.

Nickel salts can kill fish at very low concentrations. However, nickel has been found to be less toxic to some fish than copper, zinc, and iron. Nickel is present in coastal and open ocean water at concentrations in the range of 0.0001 to 0.006 mg/l although the most common values are 0.002 - 0.003 mg/l. Marine animals contain up to 0.4 mg/l and marine plants contain up to 3 mg/l. Higher nickel concentrations have been reported to cause reduction in photosynthetic activity of the giant kelp. A low concentration was found to kill oyster eggs.

For the protection of human health based on the toxic properties of nickel ingested through water and through contaminated aquatic organisms, the ambient water criterion is determined to be 0.133 mg/l.

Nickel toxicity may develop in plants from application of

sewage sludge on acid soils. Nickel has caused reduction of yields for a variety of crops including oats, mustard, turnips, and cabbage. In one study nickel decreased the yields of oats significantly at 100 mg/kg.

Whether nickel exerts a toxic effect on plants depends on several soil factors, the amount of nickel applied, and the contents of other metals in the sludge. Unlike copper and zinc, which are more available from inorganic sources than from sludge, nickel uptake by plants seems to be promoted by the presence of the organic matter in sludge. Soil treatments such as liming reduce the solubility of nickel. Toxicity of nickel to plants is enhanced in acidic soils.

Silver

Metallic silver is not considered to be toxic, but most of its salts are toxic to a large number of organisms. Upon ingestion by humans, many silver salts are absorbed in the circulatory system and deposited in various body tissues, resulting in generalized or sometimes localized gray pigmentation of the skin and mucous membranes known as argyria. There is no known method for removing silver from the tissues once it is deposited, and the effect is cumulative.

Silver is recognized as a bactericide and doses from 0.000001 to 0.0005 mg/l have been reported as sufficient to sterilize water. The criterion for ambient water to protect

human health from the toxic properties of silver ingested through water and through contaminated aquatic organisms is 0.010 mg/l.

The chronic toxic effects of silver on the aquatic environment have not been given as much attention as many other heavy metals. Data from existing literature support the fact that silver is nearly the most toxic of the heavy metals, there are insufficient data to adequately evaluate even the effects of hardness on silver toxicity. There are no data available on the toxicity of different forms of silver.

Cyanides

Cyanides are among the most toxic of pollutants commonly observed in industrial wastewaters. Introduction of cyanide into industrial processes is usually by dissolution of potassium cyanide (KCN) or sodium cyanide (NaCN) in process waters. However, hydrogen cyanide (HCN) formed when the above salts are dissolved in water, is probably the most acutely lethal compound.

The relationship of pH to hydrogen cyanide formation is very important. As pH is lowered to below 7, more than 99 percent of the cyanide is present as HCN and less than 1 percent as cyanide ions. Thus, at neutral pH, that of most living organisms, the more toxic form of cyanide prevails.

Cyanide ions combine with numerous heavy metal ions to form complexes. The complexes are in equilibrium with

HCN. Thus, the stability of the metal-cyanide complex and the pH determine the concentration of HCN. Stability of the metal-cyanide anion complexes is extremely variable. Those formed with zinc, copper, and cadmium are not stable--they rapidly dissociate, with production of HCN, in near neutral or acid waters. Some of the complexes are extremely stable. Cobaltocyanide is very resistant to acid distillation in the laboratory. Iron cyanide complexes are also stable, but undergo photodecomposition to give HCN upon exposure to sunlight. Synergistic effects have been demonstrated for the metal cyanide complexes making zinc, copper, and cadmium, cyanides more toxic than an equal concentration of sodium cyanide.

The toxic mechanism of cyanide is essentially an inhibition of oxygen metabolism, i.e., rendering the tissues incapable of exchanging oxygen. The cyanogen compounds are true noncumulative protoplasmic poisons. They arrest the activity of all forms of animal life. Cyanide shows a very specific type of toxic action. It inhibits the cytochrome oxidase system. This system is the one which facilitates electron transfer from reduced metabolites to molecular oxygen. The human body can convert cyanide to a non-toxic thiocyanate and eliminate it. However, if the quantity of cyanide ingested is too great at one time, the inhibition of oxygen utilization proves fatal before the detoxifying reaction reduces the cyanide concentration to a safe level.

Cyanides are more toxic to fish than to lower forms of aquatic organisms such as midge larvae, crustaceans, and mussels. Toxicity to fish is a function of chemical form and concentration, and is influenced by the rate of metabolism (temperature), the level of dissolved oxygen, and pH. In laboratory studies free cyanide concentrations ranging from 0.05 to 0.15 mg/l have been proven to be fatal to sensitive fish species including trout, bluegill, and fathead minnows. Levels above 0.2 mg/l are rapidly fatal to most fish species. Long term sublethal concentrations of cyanide as low as 0.01 mg/l have been shown to affect the ability of fish to function normally, e.g., reproduce, grow, and swim.

For the protection of human health from the toxic properties of cyanide ingested through water and through contaminated aquatic organisms, the ambient water quality criterion is determined to be 0.200 mg/l.

Phenol

Phenol exhibits acute and sub-acute toxicity in humans and laboratory animals. Acute oral doses of phenol in humans cause sudden collapse and unconsciousness by its action on the central nervous system. Death occurs by respiratory arrest. Sub-acute oral doses in mammals are rapidly absorbed then quickly distributed to various organs, then cleared from the body by urinary excretion and metabolism. Long term exposure by drinking phenol contaminated water has resulted in statistically significant increase in

reported cases of diarrhea, mouth sores, and burning of the mouth. In laboratory animals long term oral administration at low levels produced slight liver and kidney damage. No reports were found regarding carcinogenicity of phenol administered orally - all carcinogenicity studies were skin tests.

For the protection of human health from phenol ingested through water and through contaminated aquatic organisms the concentration in water should not exceed 3.4 mg/l.

Fish and other aquatic organisms demonstrated a wide range of sensitivities to phenol concentration. However, acute toxicity values were at moderate levels when compared to other organic priority pollutants.

Pentachlorophenol

Although data are available on the human toxicity effects of pentachlorophenol, interpretation of data is frequently accompanied by exposure to other wood preservatives. Additionally, experimental results and occupational exposure observations must be examined carefully to make sure that observed effects are produced by the pentachlorophenol itself and not by the by-products which usually contaminate pentachlorophenol.

Acute and chronic toxic effects of pentachlorophenol in humans are similar: muscle weakness, headache, loss of appetite, abdominal pain, weight loss, and irritation of skin, eyes, and respiratory tract. Available literature

indicates that pentachlorophenol does not accumulate in body tissues to any significant extent. Studies on laboratory animals of distribution of the compound in body tissues showed the highest levels of pentachlorophenol in liver, kidney, and intestine, while the lowest levels were in brain, fat, muscle, and bone.

Toxic effects of pentachlorophenol in aquatic organisms are much greater at pH of 6 where the ionic form predominates. Similar results were observed in mammals where oral lethal doses of pentachlorophenol were lower when the compound was administered in hydrocarbon solvents (un-ionized form) than when it was administered as the sodium salt (ionized form) in water.

For the protection of human health from the toxic properties of pentachlorophenol ingested through water and through contaminated aquatic organisms, the ambient quality criterion is determined to be 0.140 mg/l.

Vinyl Chloride

Vinyl chloride is a well-known human and animal carcinogen. Several occupational epidemiology studies in highly exposed workers have reported excess rates of liver angiosarcoma and tumors at other organ sites. Animal experiments using both inhalation and oral routes of exposure have also induced liver angiosarcoma. Because there is no recognized safe concentration for a human carcinogen, the

recommended concentration of vinyl chloride in water for maximum protection of human health is zero.

Because of its high vapor pressure vinyl chloride volatilizes rapidly from the aquatic environment. Because it is so readily volatilized, it does not undergo bioaccumulation except under extreme exposure conditions. Existing evidence indicates that it is resistant to microbial degradation.

3,3'-dichlorobenzidine

DCB has been shown to be a carcinogen in non-human mammals under controlled laboratory conditions. Exposure to DCB results in various types of sarcomas and adenocarcinomas. Tumors have been induced both locally (at the site of injection) and remotely (multi-system involvement after feeding). Experiments shown DCB to be a much less potent carcinogen in animals than the unsubstituted base (benzidine). U.S. EPA's Carcinogen Assessment Group (CAG) has evaluated 3,3'-dichlorobenzidine and has found sufficient evidence to indicate that this compound is carcinogenic. DCB was found to be acutely toxic to bluegill sunfish at levels of 0.5 mg/l or greater in the water.(12)

There are few data available on the bioconcentration, bioaccumulation, and biomagnification of DCB in the aquatic environment. DCB has been shown to be experimentally bioconcentrated by fish to a significant degree -- approximately 1150 fold. However, no DCB was detected in fish sampled from the vicinity of a DCB contaminated waste lagoon using analytical methods with sensitivities of 10 to 100 mg/kg.

Benzene

The chronic, rather than acute toxicity of benzene is important in industry. It is a recognized carcinogen of the blood-forming tissues. The exposure routes of concern are ingestion, inhalation and skin absorption through repeated exposures.

Benzene is harmful to human health according to numerous published studies. Most studies relate effects of inhaled benzene vapors. These effects include nausea, loss of muscle coordination, and excitement, followed by depression and coma. Death is usually the result of respiratory or cardiac failure. Two specific blood disorders are related to benzene exposure. One of these, acute myelogenous leukemia, represents a carcinogenic effect of benzene.

Oral administration of benzene to laboratory animals produced leukopenia, a reduction in number of leukocytes in the blood. Subcutaneous injection of benzene-oil solutions

has produced suggestive, but not conclusive, evidence of benzene carcinogenesis.

Benzene demonstrated teratogenic effects in laboratory animals, and mutagenic effects in humans and other animals.

For maximum protection of human health from the potential carcinogenic effects of exposure to benzene through ingestion of water and contaminated aquatic organisms, the ambient water concentration is zero. Concentrations of benzene estimated to result in additional lifetime cancer risk at levels of 10^{-7} , 10^{-6} , and 10^{-5} are 0.00015 mg/l, 0.0015 mg/l, and 0.015 mg/l, respectively.

Carbon Tetrachloride

Carbon tetrachloride produces a variety of toxic effects in humans. Ingestion of relatively large quantities - greater than five grams - has frequently proved fatal. Symptoms are burning sensation in the mouth, esophagus and stomach, followed by abdominal pains, nausea, diarrhea, dizziness, abnormal pulse, and coma. When death does not occur immediately, liver and kidney damage are usually found. Symptoms of chronic poisoning are not as well defined. General fatigue, headache, and anxiety have been observed, accompanied by digestive tract and kidney discomfort or pain.

Data concerning teratogenicity and mutagenicity of carbon tetrachloride are scarce and inconclusive. However, carbon tetrachloride has been demonstrated to be carcinogenic in laboratory animals. The liver was the target organ.

For the maximum protection of human health from the potential carcinogenic effects of exposure to carbon tetrachloride through ingestion of water and contaminated aquatic organisms, the ambient water concentration is zero. Concentrations of carbon tetrachloride estimated to result in additional lifetime cancer risk at risk levels of 10^{-7} , 10^{-6} , and 10^{-5} are 0.000026 mg/l, 0.00026 mg/l, and 0.0026, respectively.

Methylene Chloride

Methylene chloride is highly toxic by the inhalation route of exposure over a short period of time.

Inhaled methylene chloride acts as a central nervous nervous depressant. There is also evidence that the compound causes heart failure when large amounts are inhaled.

Methylene chloride does produce mutation in tests for this effect. In addition a bioassay recognized for its extremely high sensitivity to strong and weak carcinogens produced results which were marginally significant. Thus potential carcinogenic effects of methylene chloride are not confirmed or denied, but are under continuous study. Difficulty in conducting and interpreting the test results from the low boiling point (40°C) of methylene chloride which increases the difficulty of maintaining the compound in growth media during incubation at 37°C ; and from the difficulty of removing all impurities, some of which might themselves be carcinogenic.

For the protection of human health from the toxic properties of methylene chloride ingested through water and contaminated aquatic organisms, the ambient water criterion is 0.002 mg/l.

Trichloroethylene

Data on the effects produced by ingested TCE are limited. Most studies have been directed at inhalation exposure. Nervous system disorders and liver damage are frequent results of inhalation exposure. In the short term exposures, TCE acts as a central nervous system depressant - it was used as an anesthetic before its other long term effects were defined.

TCE has been shown to induce transformation in a highly sensitive in vitro Fischer rat embryo cell system (F1706) that is used for identifying carcinogens. Severe and persistent toxicity to the liver was recently demonstrated when TCE was shown to produce carcinoma of the liver in mouse strain B6C3F1. One systematic study of TCE exposure and the incidence of human cancer was based on 518 men exposed to TCE. The authors of that study concluded that although the cancer risk to man cannot be ruled out, exposure to low levels of TCE probably does not present a very serious and general cancer hazard.

TCE is bioconcentrated in aquatic species, making the consumption of such species by humans a significant source of TCE. For the protection of human health from the potential carcinogenic effects of exposure to trichloroethylene through ingestion of water and contaminated aquatic organisms, the ambient water concentration is zero. Concentrations of trichloroethylene estimated to result in additional lifetime cancer risk of 1 in 100,000 corresponds to an ambient water concentration of 0.00021 mg/l.

Only a very limited amount of data on the effects of TCE on freshwater aquatic life are available. One species of fish (fathead minnows) showed a loss of equilibrium at concentrations below those resulting in lethal effects.

Tetrachloroethylene

Tetrachloroethylene is highly toxic via ingestion and moderately toxic via inhalation and skin absorption as well as being carcinogenic.

The principal toxic effect of tetrachloroethylene on humans is central nervous system depression when the compound is inhaled. Headache, fatigue, sleepiness, dizziness and sensations of intoxication are reported. Severity of effects increases with vapor concentration. High integrated exposure (concentration times duration) produces kidney and liver damage. Very limited data on tetrachloroethylene ingested by laboratory animals indicate liver damage occurs

when PCE is administered by that route. Tetrachloroethylene tends to distribute to fat in mammalian bodies.

One report found in the literature suggests, but does not conclude, that tetrachloroethylene is teratogenic. Tetrachloroethylene has been demonstrated to be a liver carcinogen in B6C3-F1 mice.

For the maximum protection of human health from the potential carcinogenic effects of exposure to tetrachloroethylene through ingestion of water and contaminated aquatic organisms, the ambient water concentration is zero. Concentrations of tetrachloroethylene estimated to result in additional lifetime cancer risk levels of 10^{-7} , 10^{-6} , and 10^{-5} are 0.000020 mg/l, 0.00020 mg/l, and 0-.0020 mg/l, respectively.

Naphthalene

Naphthalene, ingested by humans, has reportedly caused vision loss (cataracts), hemolytic anemia, and occasionally, renal disease. These effects of naphthalene ingestion are confirmed by studies on laboratory animals. No carcinogenicity studies are available which can be used to demonstrate carcinogenic activity for naphthalene. Naphthalene does bioconcentrate in aquatic organisms.

For the protection of human health from the toxic properties of naphthalene ingested through water and through contaminated aquatic organisms, the ambient water criterion is determined to be 143 mg/l.

Only a limited number of studies have been conducted to determine the effects of naphthalene on aquatic organisms. The data from those studies show only moderate toxicity.

Di (2-ethylhexyl) phthalate

Di (2-ethylhexyl) phthalate is insoluble in water. For the protection of human health from the toxic properties of di(2-ethylhexyl) phthalate ingested through water and through contaminated aquatic organisms, the ambient water quality criterion is determined to be 10 mg/l.

Di-n-butyl phthalate

The water solubility of di-n-butyl phthalate at room temperature is reported to be 0.4 g/l and 4.5 g/l in two different chemistry handbooks.

For protection of human health from the toxic properties of di-n-butyl phthalate ingested through water and through contaminated aquatic organisms, the ambient water quality criterion is determined to be 5 mg/l.

Toluene

Toluene is moderately toxic by ingestion and inhalation. Because toluene is both water soluble and volatile, it may pose a threat to human health by both exposure routes, respectively. Toluene is volatile (vapor pressure of toluene is 36.7 mm at 30°C); handling and disposal of the waste may thus pose an inhalation hazard. If the waste is disposed in an unsecured landfill the toluene may be solubilized from the waste (the

water solubility of toluene is 535 mg/l, and it is miscible with a variety of organic solvents) by rainfall and contaminate underlying potable groundwater sources with may pose a hazard to human health when the water is ingested.

Most data on the effects of toluene in human and other mammals have been based on inhalation exposure or dermal contact studies. There appear to be no reports of oral administration of toluene on human subjects. A long term toxicity study on female rats revealed no adverse effects on growth, mortality, appearance and behavior, organ to body weight ratios, blood-urea nitrogen level, bone marrow counts, peripheral blood counts, or morphology of major organs. The effects of inhaled toluene on the central nervous system, both at high and low concentrations, have been studied in humans and animals. However, ingested toluene is expected to be handled differently by the body because it is absorbed more slowly and must first pass through the liver before reaching the nervous system. . Toluene is extensively and rapidly metabolized in the liver. One of the principal metabolic products of toluene is benzoic acid, which itself seems to have little potential to produce tissue injury.

Toluene has been found in fish caught in harbor waters in the vicinity of petroleum and petrochemical plants. Bioconcentration studies have not been conducted, but bioconcentration factors have been calculated on the basis of the octanol-water partition coefficient.

For the protection of human health from the toxic properties of toluene ingested through water and through contaminated aquatic organisms, the ambient water criterion is determined to be 12.4 mg/l.

1,1,1-Trichloroethane

Most human toxicity data for 1,1,1-trichloroethane relates to inhalation and dermal exposure routes. Limited data are available for determining toxicity of ingested 1,1,1-trichloroethane, and those data are all for the compound itself not solutions in water. No data are available regarding its toxicity to fish and aquatic organisms. For the protection of human health from the toxic properties of 1,1,1-trichloroethane ingested through the consumption of water and fish, the ambient water criterion is 15.7 mg/l. The criterion is based on bioassay for possibly carcinogenicity.

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Response to Comments to the Proposed Rule

Two commenters responding to the proposed Hazardous Waste Guidelines and Regulations (43 FR 58946, December 18, 1978) objected to the classification of paint wastes, stating that EPA had been "overly broad" in its classification (5). Dupont commented that the diversity of products, product types, and different chemical formulations makes the listing of paint wastes (specifically "water-based paint wastes") impossible without a detailed listing of the waste generated by the manufacture of various paint products.

Based on the information presented in this document, the Agency believes these listed wastes are typically or frequently hazardous. Individual generators can, of course, petition to delist their waste. In further response, EPA cites information considered by Effluent Guidelines Division for subcategorization of the paint industry (1):

EPA considered the following factors in determining whether differences within the paint industry might require separate limitations:

1. Raw materials and products
2. Production Methods
3. Size and age of production facilities
4. Wastewater characteristics
5. Tank cleaning techniques.

The Agency concluded that tank cleaning techniques offer appropriate basis for subcategorization; examination of the other four factors proved to be inappropriate for subcategori-

zation. (See Reference 1, pp. 53-55).

A second comment was that wastewater treatment sludge from latex paint production is not hazardous because extracts of the waste do not exceed 10 times the drinking water standards. National Paint and Coatings Association submitted extraction data on seven samples of latex sludge using the TEP ("Toxicant Extraction Procedure"--an extraction test which was a pre-proposal version of the EP). Test results show heavy metals in the extract to be less than 100 times the drinking water standard for those metals.

As far as differentiating latex paint wastewater treatment sludge from other wastewater treatment sludge in the industry, EPA cannot do so because 1) only 4.8% of paint manufacturers produce exclusively water-based paint and 2) when evaluating factor #4 listed above, EPA found that no specific segment of the industry has a significantly different quality or quantity of wastewater, and therefore concludes the same for the wastewater treatment sludge. In addition, EPA is listing wastewater treatment sludge for factors other than EP toxicity, including levels of heavy metals in the sludge, total quantities of the waste produced and disposed per year, and, perhaps most significantly the presence of toxic organics in the sludge.

Organic Chemicals

LISTING BACKGROUND DOCUMENT

NITROBENZENE/ANILINE PRODUCTION

Distillation Bottoms from Aniline Production (T)

Combined Wastewater Streams Generated from Nitrobenzene/
Aniline Production (T)*

Process Residues from Aniline Extraction (T)*

I. Summary of Basis for Listing

The first listed waste is the distillation bottom residue from the purification of aniline by distillation. The second listed waste is the combined process wastewater streams from the co-production of nitrobenzene and aniline. These waste streams contain toxic nitrogenous organic materials, and the wastewater stream is likely to contain benzene as well. The third listed waste stream results from the extraction step in aniline production, and may or may not be combined with other process waters. This listing covers the uncombined waste streams.

The Administrator has determined that still bottoms from aniline distillation, process residues from aniline extraction (when generated as a separate waste stream and not combined with other process wastewater streams), and wastewater generated from nitrobenzene and aniline production are solid wastes which may pose a substantial present or potential hazard to

*These waste streams were not included in the initial listing, and are initially proposed in the present document.

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 distillation bottoms contain aniline, diphenylamine, nitrobenzene, and phenylenediamine while the combined wastewater stream contains these constituents and usually contains benzene as well.* The process residues from aniline extraction, if disposed of separately, contains aniline, nitrobenzene and phenylenediamine. All of these constituents are toxic. Benzene is a known human carcinogen. Aniline, diphenylamine and phenylenediamine are carcinogenic to laboratory animals. Diphenylamine is expected to bioaccumulate.
- 2) Current disposal practices of these wastes are not well documented. However, there is a high potential for contaminating groundwater by leaching from waste treatment lagoons or landfills that are not properly designed or operated, since these constituents have high migratory potential, and some have proven mobile and persistent in actual waste management practice. In addition, under certain conditions, release to the atmosphere by volatilization poses a risk of inhalation of aniline and nitrobenzene.
- 3) In a damage incident involving improperly managed aniline distillation bottoms, waste oils were contaminated with nitrobenzene from the distillation residues and spread over roads, posing the risk of human exposure to dangerously high concentrations of nitrobenzene. This waste has thus proven capable of posing a potential substantial hazard in actual waste management practice.
- 4) The State of Texas regulates distillation bottoms from aniline production as a hazardous waste.

* Aniline, diphenylamine and phenylenediamine are not presently listed in Appendix VIII to Part 261. An amendment to Appendix VIII to add these constituents is being prepared concurrently with this listing document.

- 5) Total potential loadings of benzene and aniline in the wastewater stream from the production of nitrobenzene and aniline could be as high as 9.5 kkg and 150 kkg annually, quantities believed by the Agency to be quite significant in view of these compounds' adverse health effects.

II. Sources of the Waste and Typical Disposal Practices

A. Profile of the Industry

Nitrobenzene and aniline are major chemical intermediates; the actual nameplate capacity was reported as 557,000 kkg⁽²⁵⁾ and 313,000 kkg respectively.⁽²⁾ The U.S. International Trade Commission lists aniline as the sixth largest volume intermediate in terms of 1978 production.⁽¹⁾ Table 1 lists the facilities producing nitrobenzene and aniline, and their production capacities. As is indicated, most facilities produce both nitrobenzene and aniline. In fact, 97% of nitrobenzene produced is used for the synthesis of aniline. The balance is purified for use chiefly as a solvent, or in the manufacture of pharmaceuticals, dyes and photographic chemicals.

United States production of aniline is increasing. Production levels were 151,000 kkg in 1969, 186,000 kkg in 1972, 187,000 kkg in 1975,⁽³⁾ and 270,000 kkg in 1978.⁽¹⁾ Aniline production capacity is anticipated to reach 450,000 kkg in 1980. Most aniline (about 40%) is used for the production of methylene diisocyanate, an intermediate used in the manufacture of urethanes; another 35% is used in the

Table 1

PRODUCER LOCATIONS AND PRODUCTION CAPACITIES

MANUFACTURER	FACILITY	PRODUCTION CAPACITY (10 ³ kg)	
		1978 Nitrobenzene(25)	1977 Aniline(2)
American Cyanamid Co.	Bound Brook, NJ	48	27
American Cyanamid Co.	Willow Island	33	28
E. I. Dupont de Nemours & Company, Inc.	Beaumont, TX	140	104
E. I. Dupont de Nemours & Company, Inc.	Gibbstown, NJ	90	59
First Mississippi Corp.	Pascaquola, MS	151	45
Mallinkrodt Corp.	Raleigh, NC	0	10
Mobay Chemical Corp.	New Martinsville, WV	61	45
Rubicon Chemicals, Inc.	Geismar, LA	<u>34</u>	<u>27</u>
		557	340

synthesis of rubber chemicals.⁽²⁾ The remainder is mainly used in the manufacture of dyes and drugs.

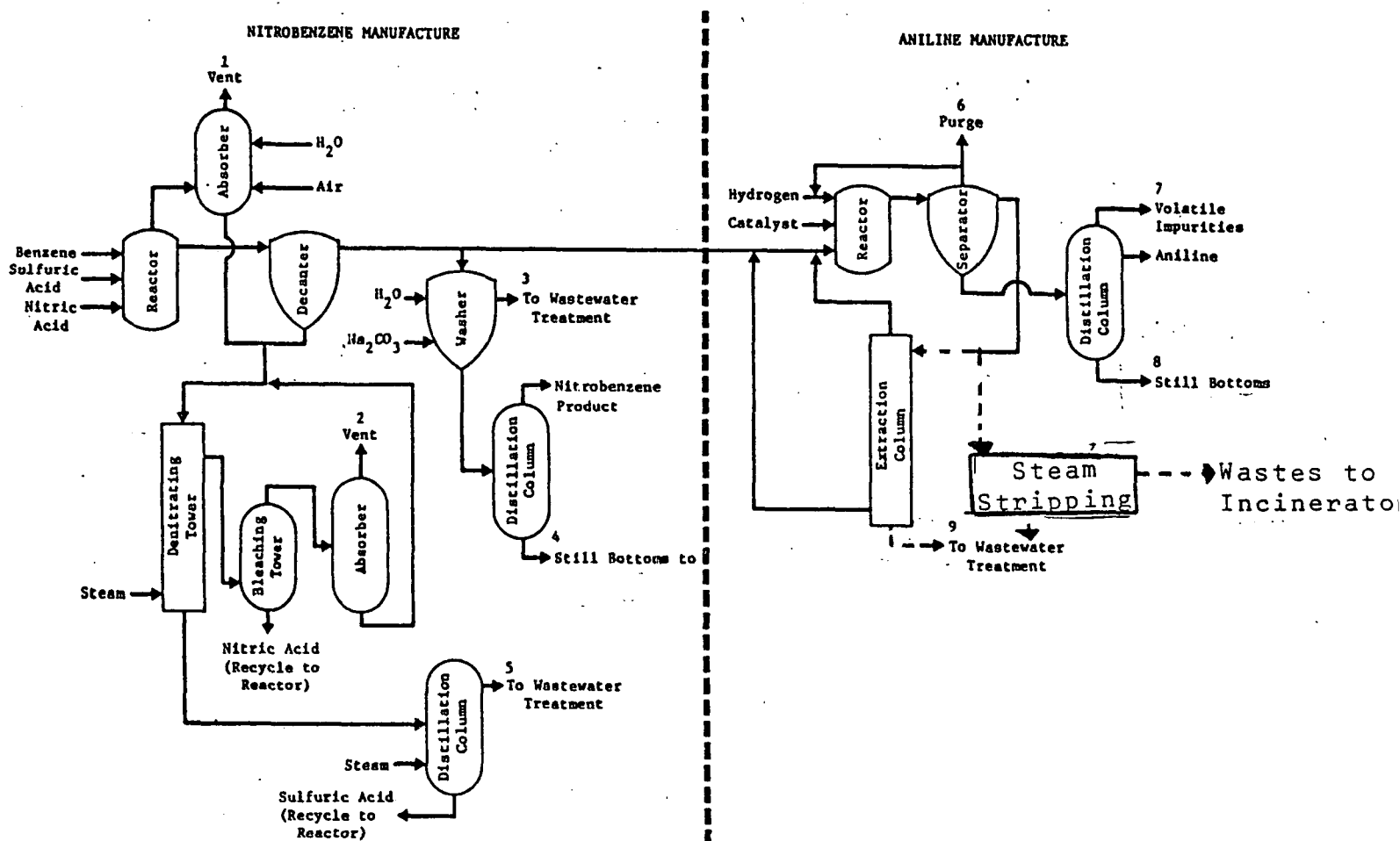
B. Manufacturing Process⁽²⁾

1. Manufacture of Nitrobenzene

Nitrobenzene is made by the direct nitration of benzene using a sulfuric-nitric acid mixture. In the most common continuous phase process, benzene is nitrated with an aqueous mixture of sulfuric acid (53 to 60 mole percent) and nitric acid (39 to 32 mole percent) at atmospheric pressure and temperatures between 45 to 90°C. Yields are typically better than 98 percent. This process (see Figure 1) is carried out in vented stainless steel vessels equipped with high speed agitators and cooling coils. Average residence time is approximately 8 to 10 minutes. Nitrobenzene is continuously drawn from the side of the reactor and separated in a decanter. Once separated, this "crude" nitrobenzene is reportedly used directly in the manufacture of aniline.

If pure nitrobenzene is required, the product is washed first with water and subsequently⁶ with an alkaline solution (generally either a sodium carbonate or sodium hydroxide solution) in small vessels equipped with high speed mechanical agitators, and then distilled. The wastewater resulting from the washing operation (stream 3 in Figure 1), is one component of the waterborne waste stream of concern in this document.

FIGURE 1
SIGNIFICANT POLLUTANTS FROM
NITROBENZENE/ANILINE MANUFACTURE (MODIFIED FROM (2))



Point 1*

Benzene, Nitroalkanes, Nitrobenzene, Nitrogen Oxides

Point 2*

Benzene, Nitroalkanes, Nitrobenzene, Nitrogen Oxides

Point 3

Benzene, Benzoic Acid, Carboxylic Acids, Nitrates, Nitrites, Nitrobenzene, Nitrophenol

Point 4**

Dinitrobenzene, Nitrobenzene, Nitrophenol, Nitrogen Containing High Molecular Weight Polymers, Polycarboxylic Acid, Dinitrotoluene

FIGURE 1 CONTINUED

Point 5

Benzene, Nitrobenzene, Nitrophenol, Polycarboxylic Acid, Nitrogen Containing High Molecular Weight Polymers

Point 6*

Aniline, Carbon Monoxide, Hydrogen, Methene, Nitrobenzene

Point 7*

Cyclohexylamine, Volatile Amines, Water

Point 8*

Aminophenols, Azepins, Diphenylamine, Nitrobenzene, Phenylenediamine, Nitrogen Containing High Molecular Weight Polymers

Point 9

Aminophenol, Aniline, Nitrobenzene, Phenylenediamine, Water Soluble Amines

* Emitted to air and therefore not subject to RCRA.

**This waste was listed in the May 19, 1980 promulgation (see "Nitrobenzene Background Document" for details).

Figure 1 to be inserted here.

Recovery of spent acid (A in Figure 1), is essential from the standpoint of economical operation. Generally, unreacted nitric acid is extracted from the spent acid by steam stripping (denitrating tower). The bottom product, dilute sulfuric acid (60 percent by weight), is then concentrated by distillation (sulfuric acid concentrator) and recycled to the reactor as shown, or used in other manufacturing operations. Nitric acid removed overhead from the denitrating tower is bleached with air to remove nitrogen oxide and subsequently recycled to the reactor. The overhead nitrogen oxides from the bleacher are scrubbed with water and recycled to the denitrating tower.* The waste resulting from acid recovery (number 5 in Figure 1) is another component of the aqueous waste stream of concern in this document.

2. Production of Aniline(2,3)

In the U.S., aniline production is based almost exclusively on vapor phase reduction of nitrobenzene in the presence of a copper catalyst. This process is also illustrated in Figure 1. With the exception of one facility (Mallinkrodt, Inc.), the nitrobenzene feedstock is produced on site.⁽²⁾ The nitrobenzene is vaporized in a stream of hydrogen and introduced into the reactor. The crude product mixture (aniline, hydrogen and water) leaving the reactor is condensed and separated from

*Another approach to spent acid recovery uses benzene, rather than steam, to strip nitric acid from spent acid in the denitrating tower. The nitric acid is thus dissolved in the benzene and fed to the reactor. The remaining sulfuric acid is concentrated as before.

the gas stream. Most of this gas stream is compressed and recycled to the reactor, but, to prevent build-up of gaseous impurities in the reactor, some gas is purged. The two-phase (aqueous and organic) reactor product mixture is separated. The lower organic phase (stream B, Figure 1), consisting principally of aniline, up to 5 percent nitrobenzene, and 5 percent water,⁽²⁾ is purified by two stage distillation. In the crude still, aniline and water are removed overhead, while higher boiling organic impurities, such as nitrobenzene, remain in the still bottoms (noted as 8, Figure 1). In a finishing distillation step, the overhead product from the crude still is purified to 99% specification, and the bottoms from this finishing distillation step are combined with the crude distillation bottoms. (This process is shown as a single distillation in Figure 1.)⁽³⁾

Several methods are used to recover aniline from the aqueous phase of the separator (C in Figure 1). Aniline may for instance be concentrated from this stream by steam stripping. The resulting enriched aniline/water mixture is then incinerated. This latter waste stream is not included within the present listing, although it may be listed in the future. The Agency solicits information as to the composition of this waste and risks associated with its improper disposal.

At some facilities aniline is recovered by countercurrent extraction with nitrobenzene. Recovered aniline and nitrobenzene are recycled to the reactor. In either case (i.e., if either

extraction or steam stripping is used), the residual waste stream (9 in Figure 1) ordinarily is directed to wastewater treatment with other process wastewater streams. This is the third component of the waterborne waste stream of concern in this document. In some facilities, the residues from the extraction step are not combined with other process wastewaters. In such cases, the listing includes the separate wastewater stream from the extraction step.

C. Waste Generation and Management

The listed wastes consist of still bottoms from the distillation of aniline (Point 8, Figure 1) and the wastewater streams generated from nitrobenzene/aniline manufacture (points 3, 5 and 9 of Figure 1), which are most often combined before wastewater treatment. (Wastes from the aniline extraction step are listed when disposed of separately, as discussed above.)

On the basis of process chemistry assumptions set forth in (2), the aniline distillation bottoms are expected to contain nitrobenzene, aniline, diphenylamine, and phenylenediamine. While precise concentrations are unknown, concentrations of nitrobenzene are expected to be quite high, since the organic phase prior to distillation consists of 5 percent nitrobenzene, most of which would be expected to be (and is intended to be) removed by distillation. A damage incident involving this waste (described at pp. 14-15 below) likewise suggests that nitrobenzene concentrations may be quite substantial.

The volume of aniline still bottoms and the present practices of the industry with regard to their disposal are not well defined. The most common disposal method for distillation bottoms is storage in drums in private landfills.(27) Some of these wastes are apparently utilized for their acid-neutralizing capacity in drilling operations.(4)

The wastewater stream components from nitrobenzene/aniline manufacture include: the nitrobenzene washwater (Point 3), the acid distillation column overhead (point 5) and the aniline recovery stream (point 9). Based on a knowledge of process chemistry, these streams are estimated to contain the pollutants indicated in Figure 1. Most manufacturers combine these waste lines prior to treatment.(2) Table 2 lists typical concentrations of selected pollutants found in combined nitrobenzene/aniline waste streams, as reported by two manufacturers.(2)

A variety of wastewater treatment methods are applied, and it is not known to what extent these are successful in removing the toxic chemicals from the listed waste. The following treatment methods have been reported:(2) steam stripping, carbon adsorption, aerated lagoon, biological contact, clarification, equalization, activated sludge, stabilization pond, land application, and subsurface disposal.

As noted above, the waste waters from the extraction step of aniline production are not always combined with other process wastewater streams. When disposed of separately,

Table 2

Characterization of Raw Waste Loading From
Nitrobenzene/Aniline Manufacture(2)

	kg/kg aniline product			kgg/yr*
	<u>Avg.</u>	<u>Min.</u>	<u>Max.</u>	<u>Max.</u>
Aniline	0.067	0.005	0.49	150
Benzene	0.005	0	0.031	9.5
Nitrobenzene	0.002	0	0.012	3.7

In addition to the above pollutants whose identity was quantitatively confirmed, anisophenol, benzoic acid, nitrophenol, and phenylene diamine as well as nitrates and nitrites are estimated⁽²⁾ to occur. Of these constituents the wastewater loading data show that at least aniline, benzene and nitrobenzene are present in substantial concentrations, and generated in significant quantities annually.

*Obtained by multiplying the maximal value by the 340,000 kkg by 90% of annual aniline nameplate production capacity (since plants rarely operate at 100% of capacity).

this waste stream is expected to contain aniline, phenylenediamine and nitrobenzene as constituents of concern.(2)

III. Discussion of Basis for Listing

A. Hazards Posed by the Waste

On the basis of available information, it is apparent that the listed wastes contain toxic organic materials, including nitrobenzene, aniline, diphenylamine and phenylenediamine, and (for the combined wastewaters) benzene. These constituents are all toxic, and all but nitrobenzene are experimental or (in the case of benzene) known carcinogens. All of these constituents are projected to have migratory potential and to be mobile and persistent in ground and surface water (Appendix B), so that they can create a substantial hazard if disposal facilities are not properly designed and operated. Aniline, nitrobenzene and phenylenediamine are quite soluble (solubility 34,000, 38,000 ppm and 1900 ppm respectively),(6) and thus can easily migrate through unsaturated sandy soils. Diphenylamine is also significantly soluble for purposes of risk of chronic exposure (300 ppm (6)). Furthermore, the solubility of amines such as aniline and phenylendiamine increases significantly under conditions which are more acidic than their acid dissociation constant (pKa is 6.0 for phenylenediamine). Since the pH of the rainfall in the United States presently ranges from 4.0 - 5.0(9,22), residues of aniline and phenylenediamine can be expected to

leach to surface and groundwater if these wastes are improperly transported, treated, stored, disposed of, or otherwise managed.

Present waste disposal practices may be inadequate to prevent waste migration. Certainly, improper management may result in release of harmful constituents, particularly in view of the properties of the waste constituents as described above. For instance, if this waste should be exposed to an environment subject to acid rainfall, disposed residues containing phenylenediamine contacted by acid rainfall can be expected to leach and to migrate to surface and groundwater.

Further, if this waste is treated in a lagoon, even under relatively mild environmental conditions, the harmful constituents can be expected to leach from the waste, as a result of their moderate to extreme water solubility properties. Once released from the matrix of the waste, these constituents could migrate from the waste and contaminate groundwater. Nitrobenzene, for example, has proven mobile and persistent in two major damage incidents involving waste disposal at the Monsanto Chemical dump in East St. Louis and at the LaBounty dump in Charles City, Iowa.(10)

Another potential hazard associated with lagoon treatment of this waste would be the volatilization of compounds with appreciable vapor pressure such as benzene into the atmosphere, thus posing a hazard via inhalation. Benzene has proven capable of migration and persistence via an air exposure

pathway in many actual damage incidents, Love Canal being the most notorious.

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 many of the subject production facilities are located in regions of significant rainfall (LA, 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.)

A special hazard posed by these subject wastes is the possibility of the formation over time of highly carcinogenic nitrosamines from some of their constituents.⁽²⁾ Aniline and other amines (most importantly secondary amines) as well as nitrites are thought to be present in these wastes (Figure 1). These substances may react to form nitrosamines, especially under acidic conditions. Such conditions might result as a consequence of co-disposal of the listed wastes with acidic wastes, or under conditions of continued acid rainfall.

Improperly managed aniline distillation bottoms have been involved in at least one damage incident.⁽²³⁾ From 1976

through November 1978, contaminated waste oils were used as dust suppressants on roads throughout East Texas. The chief source of contamination were aniline tars (still bottoms) from aniline production*, generated by Dupont's Beaumont facility. These still bottoms were sent to Browning-Ferris Industries Chemical Services, Inc., a state permitted waste management facility, which proceeded impermissibly to mix the wastes with waste oil, which oil was used indiscriminately as a road dust suppressant. Nitrobenzene levels in contaminated soil varied, and were as high as 21,000 ppm. Most of the concentrations were deemed by state environmental officials as more than sufficient to cause substantial harm. The danger was discovered before occurrence of known harm, and Browning-Ferris was ordered to remove approximately 10,000 cubic yards of contaminated material from one subdivision, and additional amounts of material from four additional subdivisions.(23)

This incident not only illustrates the potential for substantial harm if this waste is disposed of improperly, but also suggests strongly that the aniline distillation residues may contain very high concentrations of nitrobenzene, in light of the substantial concentrations found in the contaminated road oil. Furthermore, aniline distillation bottoms are

* The waste oils were heavily contaminated with nitrobenzene, and the only source of nitrobenzene in wastes accepted by Browning-Ferris were aniline distillation wastes. (23 at p. 17.)

regulated as hazardous wastes (termed 'Class I wastes' under the state waste management system) by the State of Texas (23), another indication of their potential for hazard.

B. Health and Ecological Effects of Waste Constituents of Concern

Benzene

Acute exposure to high concentrations of benzene causes central nervous system depression (euphoria, nausea, staggering gait and coma). Inhalation of lower amounts produces dizziness, headache and nausea. EPA's Carcinogen Assessment Group has designated benzene as a human carcinogen (leukemogen).

Benzene demonstrated teratogenic effects in laboratory animals. Chromosomal changes have also been demonstrated in workers exposed to benzene.(28)

For maximum protection of human health from the potential carcinogenic effects of exposure to benzene through ingestion of water and contaminated aquatic organisms, the ambient water concentration is zero. Concentrations of benzene estimated by the Agency's Carcinogen Assessment Group to result in additional lifetime cancer risk at levels of 10^{-7} , 10^{-6} , and 10^{-5} are 0.00015 mg/l, 0.0015 mg/l, and 0.015 mg/l, respectively.(29)

Because benzene is soluble in water, it could be leached from the wastewater treatment sludge which would be generated from treatment of the combined wastewaters, in a landfill situation and pose a threat to groundwater supplies. Because

it is also volatile (vapor pressure = 100 mm at 26.1°C (Appendix B.)), it may pose an inhalation hazard during handling in transportation and disposal. Additional information on the adverse health and environmental effects of benzene can be found in Appendix A.

Nitrobenzene

Nitrobenzene has toxic reproductive effects: in rats it delays embryogenesis, alters normal placentation, and produces abnormal fetuses (14); changes in the tissues of the chorion and placenta have been reported in women exposed to nitrobenzene (15). Nitrobenzene has been listed as a Priority Pollutant in accordance with §307(a) of the Clean Water Act of 1977.

With present data, it is not possible to fully estimate its aquatic fate. Hydrolysis and volatilization from water are considered unlikely. Adsorption onto humus and clay, and subsequent production by weathering and biological action, of (carcinogenic) benzidine and diphenylhydrazine could be a major fate pathway (12). Nitrobenzene is neither stored nor ecologically magnified, but is resistant to degradation by soil microflora (11, 12). In mammalian systems nitrobenzene is metabolized to aniline, nitrophenol, p-hydroxyaniline and other metabolites, which are excreted in urine, but such metabolism in man is slower by an order of magnitude than in animals (13).

The criterion to protect freshwater aquatic life is 480 ug/l (24 hour average). The occupational exposure limit

(OSHA) is 5 mg/m³ (skin, 8 hr TWA). The American Conference of Governmental Industrial Hygienists (ACGIH) threshold limit for industrial exposure to nitrobenzene is 1 ppm.(23) Additional information on the adverse health effects of nitrobenzene can be found in Appendix A.

Aniline

Aniline is an experimental carcinogen (18). Its absorption causes anoxia due to the formation of methemoglobin, but significant chronic problems (other than animal carcinogenicity) have not been demonstrated. Human exposure to vapor concentrations of mm has been observed to cause slight symptoms.(30) Rapid absorption through the intact skin is frequently the route of entry.(16,30) Cyanosis is the most prominent outward symptom of aniline intoxication.(8) At 0.4 mg/l aniline is toxic to Daphnia (8). OSHA's PEL for aniline is 19 mg/m³ (skin, 8 hr TWA)(17). Additional information on the adverse health effects of aniline can be found in Appendix A.

Phenylenediamine

Phenylenediamine is a highly toxic substance (18), continued exposure to which can cause liver injury. It is a suspected carcinogen and teratogen (18). Of the three isomers, the p-substituted compound is by far the more toxic (19). The relative concentrations of these isomers in the listed waste are not known. The oral toxicity for human beings is high (LD₁₀ = 50 mg/kg (19)), so the high water solubility of this compound is worr some. Phenylenediamine is listed

by DOT as a hazardous substance (ORM-A), and the OSHA PEL is 0.1 mg/m³(8 hr TWA) (17).

Diphenylamine

Diphenylamine is an experimental carcinogen and teratogen (19). Chronic exposure to diphenylamine induces cystic lesions in the chicken⁽²⁰⁾ and the rat.⁽²⁴⁾ The American Conference of Industrial Hygienists has established 10 mg/m³ as an acceptable TLV for occupational exposure (21). Diphenylamine can also be expected to bioaccumulate, due to a high octanol/water partition co-efficient of 2,200 (7).

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HAZARDOUS WASTE LISTING BACKGROUND DOCUMENT

Distillation or Fractionating Column Bottoms from Production of Chlorobenzenes (T)

Separated Aqueous Stream from the Reactor Product Washing Step in the Batch Production of Chlorobenzenes (proposed) (T)*/

Distillation or fractionation column bottoms from the ^{**/}production of chlorobenzenes, and the separated aqueous waste stream from the reactor product washing step in the batch production of chlorobenzenes, are composed of a varying mixture of chlorobenzenes (dichlorobenzene through hexachlorobenzene) and benzyl chloride, and may also contain benzene and monochlorobenzene. The Administrator has determined that these waste streams are solid wastes and as solid wastes may pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, disposed of, transported or otherwise managed. Therefore, these wastes, should be subject to appropriate management requirements under Subtitle C or RCRA. This conclusion is based on the following considerations:

1. Distillation or fractionating column bottoms from chlorobenzene production are likely to contain significant concentrations of dichlorobenzenes, trichlorobenzenes, tetrachlorobenzene, pentachloroben-

*/This waste stream was not included in the original waste listing, and thus is being initially proposed in the present document.

**/Throughout this background document, the terms 'chlorobenzene' and 'chlorinated benzene' are used synonymously.

zene and hexachlorobenzene. Benzyl chloride is also expected to be present in significant concentrations. Benzene and monochlorobenzenes may also be present in lesser concentrations depending on the efficiency of distillation. The dichlorobenzenes, trichlorobenzenes and tetrachlorobenzenes are all toxic. Hexachlorobenzene and benzene have been identified as having substantial evidence of carcinogenicity by the Carcinogen Assessment Group. Pentachlorobenzene has been reported to induce cancers in some animal species. Benzyl chloride is reportedly carcinogenic. Monochlorobenzene is toxic. All of the chlorobenzenes are also highly bioaccumulative.

2. The separated aqueous waste stream from the batch production of chlorobenzenes is believed to contain significant concentrations of benzenes, and also contains the various chlorobenzenes, and probably phenols and chlorinated phenols, some of which are carcinogens, and all of which present acute and chronic toxicity hazards.
3. These waste constituents are capable of migration, mobility and environmental persistence if managed improperly, and have caused substantial hazard in actual damage incidents. Disposal of these distillation bottoms and the aqueous waste in uncontrolled landfills, therefore, could allow migration of contaminants to ground and surface waters and release of volatile toxicants to the air, while improper incineration may result in the generation of extremely hazardous compounds such as phosgene.

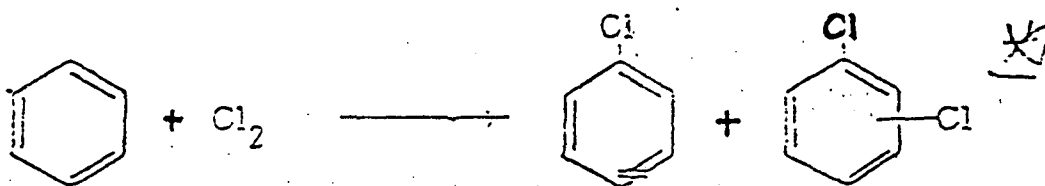
I. Industry Characterization and Manufacturing Process (1)

There are twelve chlorinated benzene compounds that can be formed during the chlorination of benzene including monochlorobenzene, three isomers of dichlorobenzenes, three of trichlorobenzenes, three of tetrachlorobenzenes, pentachlorobenzene and hexachlorobenzene.

Monochlorobenzene is the dominant commercial product; in 1978, production was approximately 134,000 metric tons.(1)

Production of ortho- and para-dichlorobenzene was estimated at 10,000 metric tons each for that same year.(1) Production of 1,2,4-trichlorobenzene was 13,000 metric tons in 1973. It is estimated that approximately the same amount was produced in 1977.(1) Statistics for other chlorobenzenes are unavailable because they have limited commercial value and their production is limited to their formation as by-products.(1) Major producers of chlorobenzenes in the United States include: Allied Chemical Corporation (Syracuse, New York); Dow Chemical Company (Midland, Michigan); Monsanto Company (Sauget, Illinois); Montrose Chemical Corporation of California (Henderson, Nevada); PPG Industries, Inc. (Natrium, West Virginia); Specialty Organics, Inc. (Irwindale, California); and Standard Chlorine Chemical Company, Inc. (Delaware City, Delaware).(2)

Chlorobenzene, dichlorobenzenes, and higher chlorinated benzenes are produced in batch and in continuous processes by direct chlorination of benzene in the presence of a Friedel Craft catalyst, such as ferric chloride, as shown in the following reaction for monochlorobenzene:



*/ 1,3-Dichlorobenzene, 1,3,5-trichlorobenzene and 1,2,3,5-tetrachlorobenzene are not produced by the method discussed below.

Because higher chlorinated benzenes always result from the direct chlorination of benzene, chlorobenzene production is a multiple product operation, i.e. a whole range of chlorinated benzenes may be produced. Product ratios are influenced by temperature, mole ratios of the feedstocks, residence time, and the catalyst. Additionally, the crude reaction product of a continuous process may be recycled to the process to achieve the desired final product mixture. Depending on the final product mixture, chlorobenzenes are purified by fractional distillation and/or crystallization. Continuous chlorination processes, in contrast to batch processes, minimize the amount of higher chlorinated products, thereby maximizing monochlorobenzene yields.

A. Production of Monochlorobenzene

1. Continuous Process (modified from Reference 1,6,7)

As shown in Figure 1 (p. 5A), in a typical continuous process for the production of chlorobenzenes, anhydrous benzene and chlorine are introduced into a reactor operating at a bottom temperature of 90-125°C and a top temperature of about 80°C. Benzene is introduced near the top of the column, and an equimolar amount of chlorine is introduced near the midpoint of the reactor. A variety of catalysts may be used, usually iron or ferric chloride impregnated on a suitable carrier.

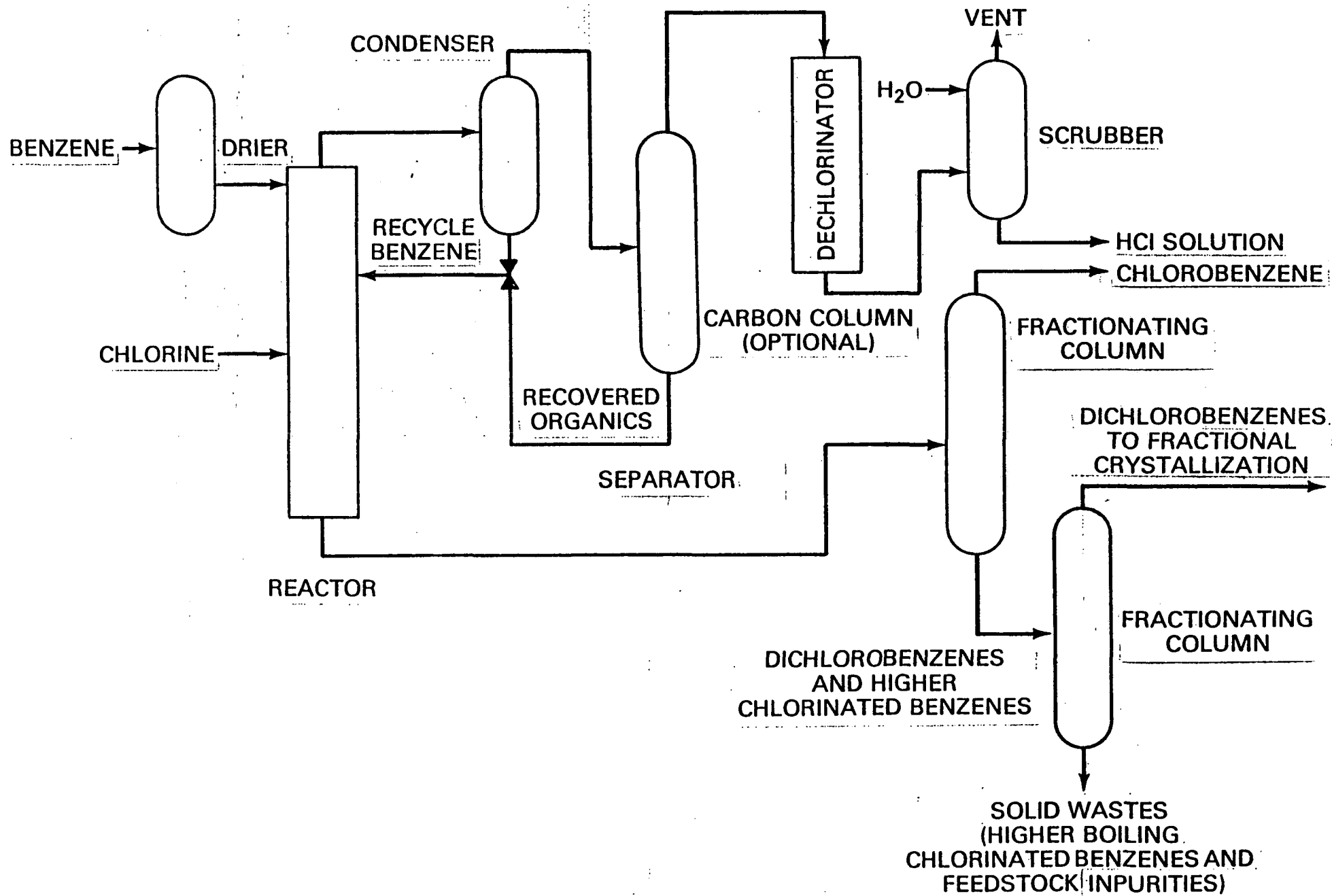


FIGURE 1
CONTINUOUS PRODUCTION OF CHLOROBENZENE (MODIFIED FROM 7)

The overhead reactor effluent consisting of hydrogen chloride and benzene passes through a condenser which condenses the benzene for recycle. Hydrogen chloride is recovered by passing the uncondensed gas through a scrubber tower containing a chlorination catalyst, thereby removing unreacted chlorine. The mixture is then passed through one or more towers in which chlorobenzenes are used to remove organic contaminants. The resultant hydrogen chloride is then recovered as either an anhydrous product or as a 30-40% aqueous solution. (If the hydrogen chloride must meet a low organic specification, a carbon column may be used prior to or after the water absorption tower.)

The bottom effluent from the reactor comprises an equilibrium mixture of benzene and mixed chlorobenzenes. To maximize monochlorobenzene production, a high recycle rate of benzene is maintained (20:1). Chlorobenzene is withdrawn at a rate equal to that at which benzene is fed and chlorinated, and flows to a fractionating column which operates at a bottom temperature of approximately 190°C and top temperature of 140°C. The higher boiling bottom products (mostly dichlorobenzenes) are continuously bled at approximately 2% of the product feed to a fractionating column for recovery of the di- and trichlorobenzenes. The wastes of concern are the bottoms from the two fractionating columns.* /

* / In some processes, this further fractionating step for recovery of higher chlorobenzenes will not occur, in which case the waste of concerns are the column bottoms from the first fractionating column.

2. Batch Process

Chlorobenzenes may also be manufactured by a batch process as shown in Figure 2. Dry benzene is charged into an agitated glass-lined or iron (steel) agitated reactor. Either iron turnings or anhydrous ferric chloride are used as a catalyst and remain in the chlorinator after each batch. Chlorine is added to the reactor at a rate to keep the temperature between 20° to 60°C. If monochlorobenzene is the desired product, the reaction temperature is maintained in the range of 20° to 30°C for 10 to 16 hours and about 60 percent of the stoichiometric requirement of chlorine used. If poly-substituted chlorobenzenes (generally dichlorobenzenes) are desired in addition to monochlorobenzene, the reaction is run at a temperature of 55° to 60°C for approximately six hours.

Hydrogen chloride is recovered in a manner similar to that of continuous processes by scrubbing with chlorobenzene to remove organic contaminants and absorbing the product gas in water to give hydrochloric acid. The chlorobenzene product is washed in an agitated reactor with an aqueous solution of sodium hydroxide (10 percent by weight). The separated aqueous layer is a separate waste stream, and is the second waste stream included in this listing.*/

*/No such aqueous stream is expected to be present in continuous processes, since during the stripping step in the continuous process (see Fig. 1) the temperature at the bottom of the condenser column already removes residual hydrogen chloride and benzene, and makes a product washing step unnecessary.

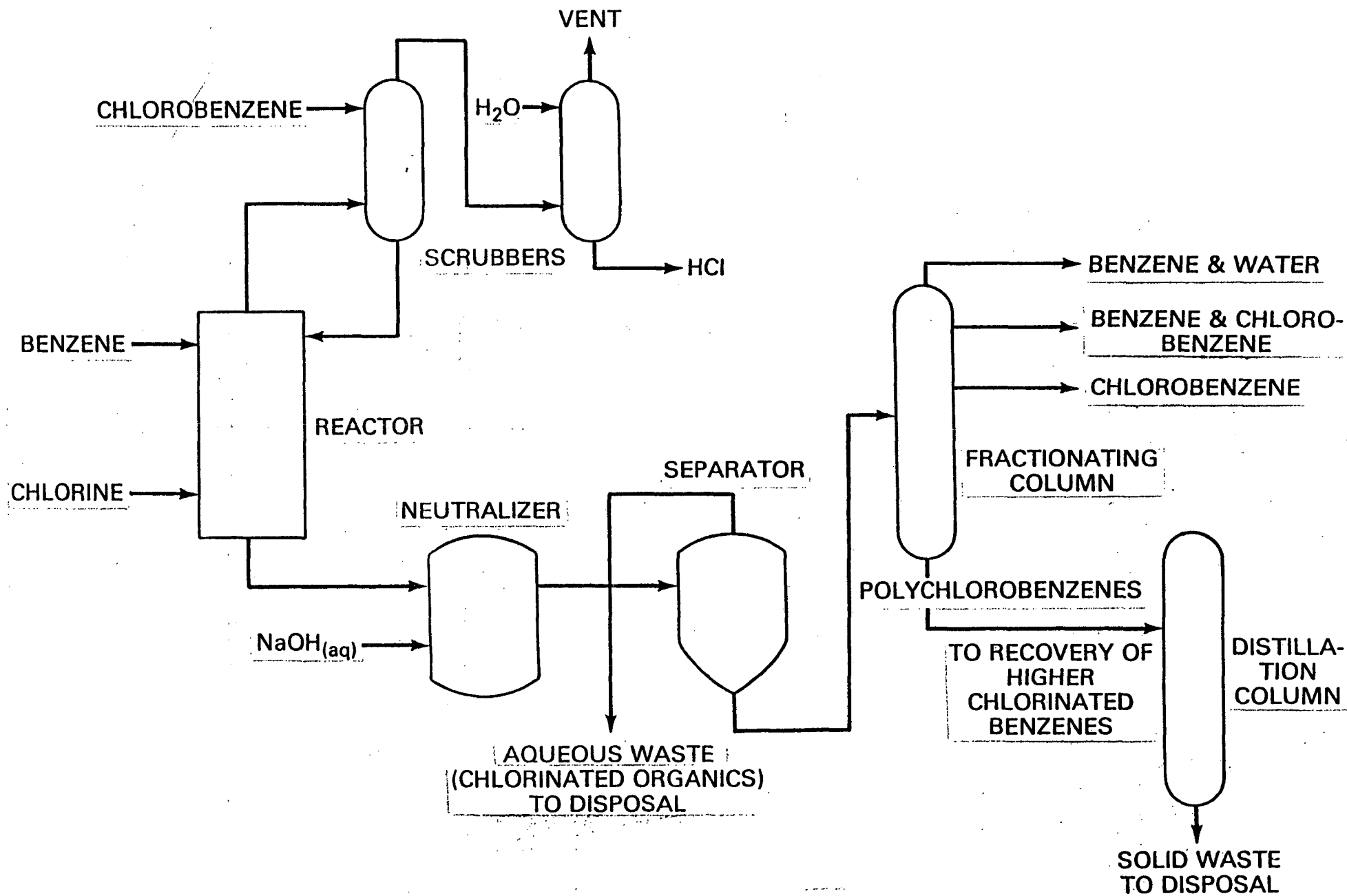


FIGURE 2
BATCH PRODUCTION OF CHLOROBENZENES (MODIFIED FROM 6)

After the neutralized organic layer is separated, it is sent to a fractionation column for product separation. A typical product distribution from fractionation is shown in Table 1 for a fully chlorinated batch for which 100 percent of the theoretical amount of the chlorine requirement for monochlorobenzene has been consumed is given.

TABLE 1

PRODUCT DISTRIBUTION OF A CHLOROBENZENE BATCH REACTION (6)

Component	% by weight
Benzene and water	3
Benzene and chlorobenzene	10
Chlorobenzene	75
Chlorobenzene and dichlorobenzene	10
Tar (trichlorobenzene and higher)	2

Most batch processes will include a further distillation step to separate higher chlorinated benzenes, particularly o- and p-dichlorobenzene and trichlorobenzene.^{*/} The chlorobenzene and dichlorobenzene fraction is usually further distilled to recover p-dichlorobenzene and o-dichlorobenzene. Trichlorobenzene may also be recovered. The tarry residue--the solid waste of concern-- consists chiefly of trichloro and higher chlorinated benzenes.

^{*/}Table 1 is a product mix prior to this second distillation step.

B. Production of Polychlorobenzenes

As noted previously, aromatic chlorination is a multiple product process; most polychlorobenzenes can be produced via processes similar to those described above. Reaction conditions are, however, likely to be somewhat different. Higher reaction temperatures, and longer reaction times and higher chlorine to benzene ratios are likely modifications. A process configuration for production of dichlorobenzenes is shown in Figure 3.

Dichlorobenzenes

Dichlorobenzenes are co-products of the production of monochlorobenzene using a ferric chloride catalyst. Separation of o- and p-dichlorobenzene is difficult by fractional distillation (bp-6°C), and so is accomplished by fractional crystallization.

Trichlorobenzenes

As noted previously, both 1,2,4- and 1,2,3-trichlorobenzene are produced as co- or by-products of the catalytic chlorination of benzene. Isomers may be separated by fractional crystallization.

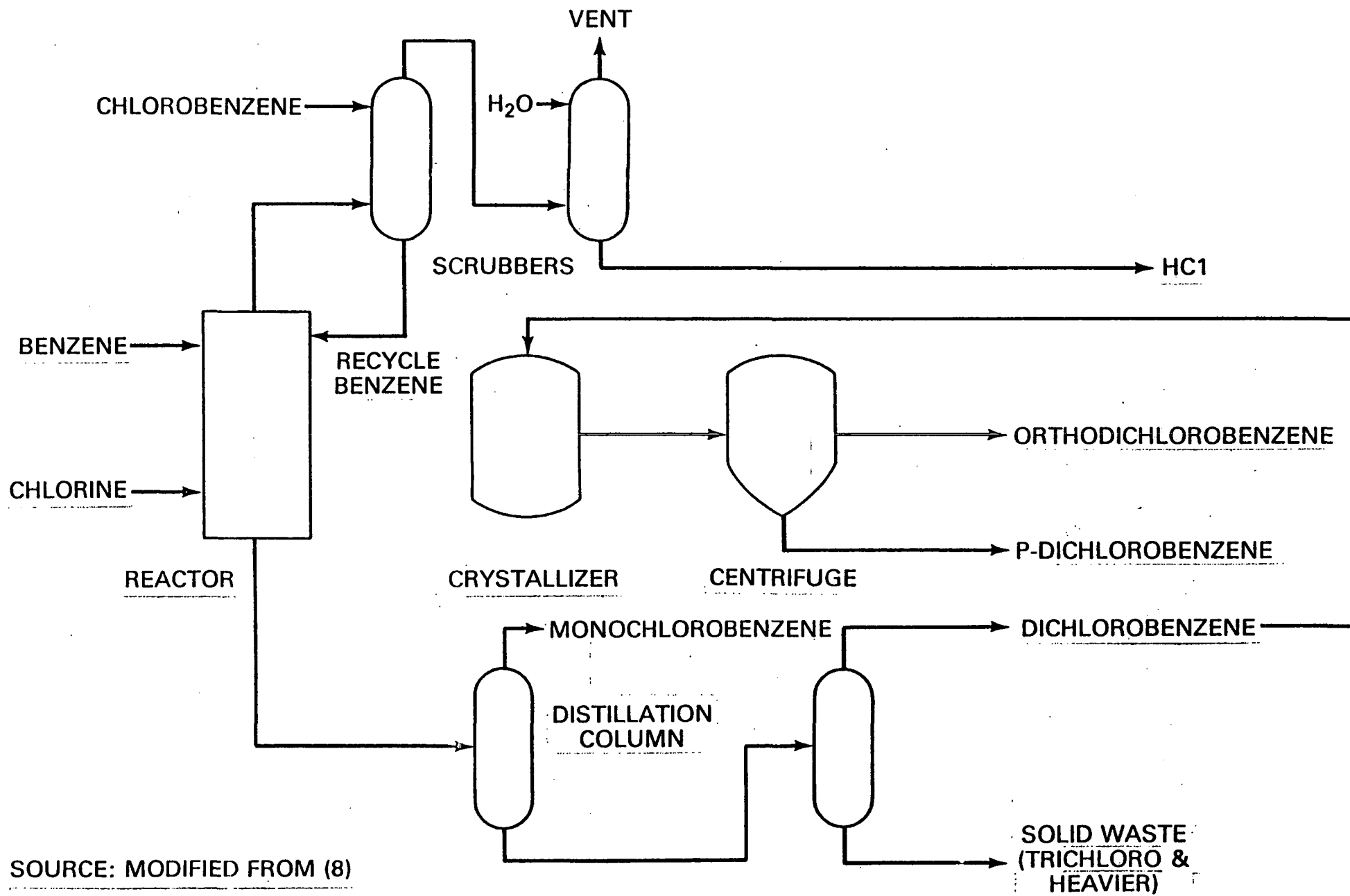
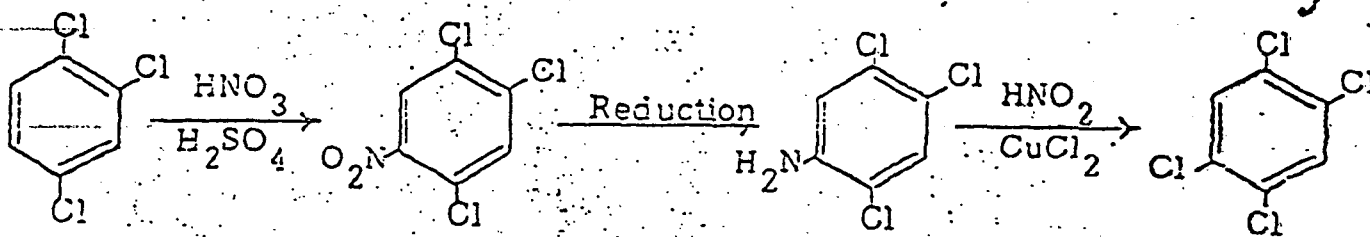


FIGURE 3
PRODUCTION OF HIGHER CHLOROBENZENES

Tetrachlorobenzenes

There are three isomeric tetrachlorobenzenes: 1,2,3,4-tetrachlorobenzene; 1,2,3,5-tetrachlorobenzene; and 1,2,4,5-tetrachlorobenzene. Of these isomers, the 1,2,4,5- isomer is a chemical and pesticide intermediate (hexachlorophene, Isobac 20, Ronnel, Silvex, and 2,4,5-T). Each isomer can be produced by catalytic chlorination using an aluminum chloride catalyst. 1,2,4,5-Tetrachlorobenzene may also be produced via the Sandmeyer reaction:



Pentachlorobenzene and Hexachlorobenzene (8,9)

Pentachlorobenzenes are formed by the chlorination of benzene in the presence of ferric or aluminum chloride at temperatures of 150 to 200°C, or by the chlorination of any of the lower chlorobenzenes.

Hexachlorobenzene is reported not to be produced commercially via catalytic (ferric chloride) chlorination of benzene. When generated as a by-product of the processes described in this document, it is not recovered and is found in the fractionating column bottoms.

II. Waste Composition and Management

1. Fractionation Bottoms

The distillation or fractionation bottoms from the production of monochlorobenzene consist primarily of the higher polychlorinated benzenes (trichlorobenzenes and higher), benzyl chloride and chlorotoluenes^{*/} resulting from the chlorination of toluene impurities in benzene feedstock, and lesser concentrations of feedstock benzene, product chlorobenzene, and dichlorobenzenes (depending on the efficiency of the fractionating step). The relative concentrations of the various chlorobenzenes in these wastes vary according to reaction conditions and the efficiency of fractionation. In general, when monochlorobenzene is the favored by-product, dichlorobenzene will probably be the most prevalent of the

^{*/}Both o- and p-chlorotoluene also are expected to be present. These constituents are not considered to be of regulatory concern because of their low chronic toxicity. Further information as to the validity of this conclusion is solicited, however.

chlorinated benzenes in the distillation residue (and in the waste if there is no subsequent distillation step to recover dichlorobenzenes as product) since benzene is being chlorinated for less time, so that smaller concentrations of tetra- to hexachlorobenzene are formed. If dichlorobenzenes are recovered as product, then trichlorobenzenes will represent the greatest fraction in the waste. When the reaction is pushed in the direction of polychlorinated benzenes, there will be more trichloro through hexachlorobenzene in the waste stream.

Waste composition, and especially the concentrations of the various chlorinated benzenes, also will vary quantitatively, although not qualitatively, depending on whether a continuous or batch production process is used. Batch processes would tend to have somewhat higher concentrations of higher chlorinated benzen^es, since benzene chlorination occurs for a longer period.

Table 1 (p. 8 above) gives an estimate of wastes resulting from a batch reaction favoring monochlorobenzene production. As noted, distillation tars are estimated to consist principally of the higher chlorinated benzenes (trichlorobenzene and higher). These tars would comprise roughly 2% by weight of the total reaction products and byproducts.

Table 2 gives a second estimate of waste composition from a batch process favoring monochlorobenzene. The polychlorinated tars are the listed hazardous wastes. Benzene and chlorobenzene would be vented to the atmosphere, since

they have lower boiling points, though small concentrations of these constituents would be expected to remain in the distillation bottoms. In addition, some dichlorobenzenes would be present from the recovery of dichlorobenzenes by subsequent distillation.

Table 2(9)

ESTIMATED LOSS OF MATERIALS DURING CHLOROBENZENE MANUFACTURE
(BATCH PROCESS)

Chemical	Source	Quantity Produced (Kg/kg monochlorobenzene)
Hydrogen Chloride (catalyst; nonhazardous)	Hot scrubber vent	0.0014
Monochlorobenzene	Dichlorobenzene Column	0.00088
Dichlorobenzenes (isomers not specified)	"	0.0037
Monochlorobenzene	Fractionating Towers	0.004
Dichlorobenzenes	"	0.0001
Polychlorinated Distillation Tars	Distillation Residues	0.044

A third reference (shown in Table 3) taken from the patent literature and involving a continuous process, shows monochlorobenzene present in fairly substantial concentrations in the solid waste, as well as the same ranges of heavier chlorinated benzenes.

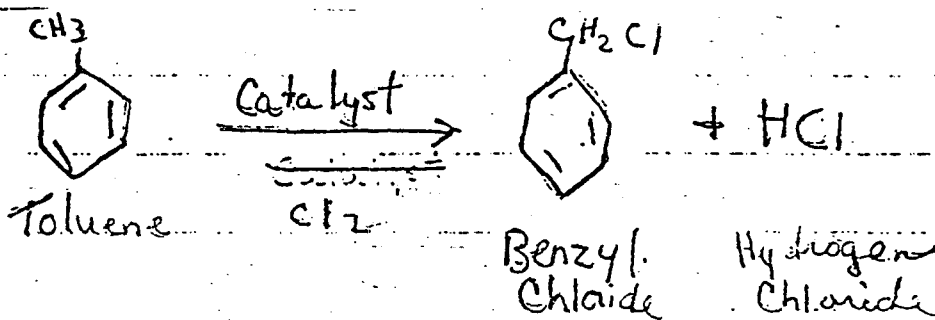
TABLE 3

ESTIMATED EMISSIONS FROM CHLOROBENZENE MANUFACTURE:
Chlorination of Benzene, Continuous Process

Species	Emissions kg/Mg		
	Air	Aqueous	Solid
Benzene			trace
Chlorobenzene			2.6
Polychlorinated benzenes			31
			33.6

Source: Derived from Hunter, W. K., Combination Reaction-Fractionation U.S. Patent 3,366,457, January, 1968.

These wastes (from both continuous and batch processes) are also expected to contain significant concentrations of benzyl chloride and o- and p-chlorotoluene resulting from chlorination of toluene impurities in benzene feedstock.*/ (As noted above, the chlorinated toluenes are not waste constituents of concern). The specific reaction pathways for these constituents are given below:



*/ Toluene is believed to be the most significant feedstock impurity. Benzene may typically contain up to 1% toluene Mellan, I. Industrial Solvents Handbook, 2nd Ed., Noyes Data Corp., Park Ridge, NJ, 1977.

These side reactions are believed to be those most likely to occur under usual conditions of benzene chlorination. Virtually all of these substances would be present in the distillation bottoms since they are high boiling chemicals that the distillation process is designed to eliminate.

2. Separated Aqueous Stream from the Reactor Product Washing Step (batch process)

The aqueous stream from the reactor product washing step in the batch production of chlorinated benzenes will contain benzene, and all of the chlorinated benzenes in solution (along with water and caustic soda used in the washing operation). Since this is an aqueous waste, concentrations of these constituents will depend on their solubilities in the somewhat alkaline wash solution. While the Agency does not presently have precise information on these compounds' solubility in basic solutions, it is not believed to differ significantly from their solubilities in water (if anything, solubilities would be slightly higher in basic solutions). Thus, the highly soluble benzene (water solubility reported at up to 1,780 ppm) would probably be the principal waste constituent, and monochlorobenzene and o- and p-dichlorobenzene would also be present in fairly significant levels (water solubilities from 79 ppm to 488 ppm respectively) would also be present in significant concentrations. The remaining chlorinated benzenes would be present at much lower levels, since their solubilities are quite low. (Solubility data is from App. B.) Phenols

could also be formed if temperatures are sufficiently high to create hydrolysis conditions, and a highly alkaline wash mixture is used. Chlorinated phenols could also be present from the phenolization of the di- and tri-chlorobenzenes, although concentrations of phenols and chlorinated phenols would probably be small.

Table 4 below shows organic contaminants found in the wastewater stream from chlorobenzene manufacture at a Dow plant.

TABLE 4

PRIORITY POLLUTANTS IDENTIFIED IN AQUEOUS WASTESTREAM FROM
PRODUCT WASHING STEP IN PRODUCTION OF CHLOROBENZENES(29)

	<u>Concentration mg/l</u>	<u>Loading kg/day</u>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>
<hr/>	<hr/>	<hr/>

*The underlined data are those obtained from proprietary reports and data files.

3. Waste Management

Waste management practices for the distillation residues generally involves disposal in on-site and off-site landfills (1). Incineration is also practiced to destroy toxic constituents (9).

The separated aqueous stream generally is sent to wastewater treatment.(1) The most feasible treatment method is activated carbon preceded by sand filtration.(1) A wastewater treatment sludge is generated which is assumed to be hazardous unless generators show otherwise. (See §261.3(a)(2)(ii).)

III. Hazards Posed by the Waste

As noted above, the distillation wastes are expected to contain significant concentrations of tri- through hexachlorobenzene, and benzyl chloride, lesser concentrations of dichlorobenzenes, and some monochlorobenzene and benzene. Furthermore, the waste stream will consist almost completely of these organic contaminants. Hexachlorobenzene and benzene have been identified as having substantial evidence of carcinogenicity by the Carcinogen Assessment Group. Pentachlorobenzene is reported to induce cancers in some animal species. Benzyl chloride is reportedly carcinogenic. The remaining constituents present acute and chronic toxicity hazards. All are priority pollutants. In addition, all of the chlorinated benzenes are very bio-accumulative (based on extremely high octanol/water partition coefficients (see pp. 23 - 28 below)) and so could pose an additional hazard even if exposure is only to small concentrations of the pollutant.

The aqueous wastestream will contain benzene, chlorobenzenes through trichlorobenzene, and (under certain conditions) certain phenols and chlorinated phenols. 2,4-dichlorophenol and 2,4,6-trichlorophenol have been identified by the Carcinogen Assessment Group as having substantial evidence of carcinogenicity. In addition, both compounds present acute and chronic toxicity hazards. 2,4,6-trichlorophenol is also mutagenic.

In light of the reported concentrations of these hazardous constituents, these waste streams are clearly of regulatory concern. Indeed, for the carcinogens in the wastes, there is no known safe level of exposure, every exposure likely giving rise to at least one cancer in a defined portion of population, regardless of exposure concentration. (EPA Water Quality Criteria, 44 Fed. Reg. 15926, 15930 (March 15, 1979).) The Agency thus requires strong assurance that these waste constituents are incapable of migration, mobility, and persistence in the event of improper management to justify not listing this class of wastes. Such assurance does not appear possible.

All of the waste constituents have proved capable of migration, of mobility through soils, and of environmental persistence in the course of actual waste management practice, creating a substantial potential for hazard. Benzene and all of the chlorinated benzenes through pentachlorobenzene have been detected in air, basement sump and solid surface samples collected in the vicinity of the Love Canal waste disposal

site in Niagra, New York.(5) Benzyl chloride has been identified as leaching from Hooker's Hyde Park site in Niagra, New York (OSW Hazardous Waste Division, Hazardous Waste Incidents, Open Files, 1978), and has been shown to persist in the atmosphere in the New Jersey area for considerable periods of time (Altshuller, A. P., Lifetimes of Organic Chemicals in the Atmosphere, Environmental Scientific Technology, 1980, in press).

Hexachlorobenzene has likewise been shown to migrate via air and groundwater pathways and to persist following migration. One notorious damage incident involving hexachlorobenzene occurred in Louisiana in the early 1970s. Exposure to hexachlorobenzene resulted via inhalation from transport of hexachlorobenzene-contaminated wastes, resulting in dangerously elevated hexachlorobenzene concentrations in humans and animals along the route. (OSW Hazardous Waste Management Division, Hazardous Waste Incidents, unpublished, Open Files, 1978.) Hexachlorobenzene has also been detected in concentrations exceeding background levels in many groundwater monitoring samples taken at various locations at a chosen chemical company dump. (1 at Table 7.2.)

The phenols and chlorinated phenols present in the waste water stream also are capable of migration, mobility, and persistence. Phenol and 2-chlorophenol are extremely soluble in water (App. B) and, although subject to biodegradation (id.),

could persist for long periods of time in the abiotic conditions characteristic of most aquifers. Both 2,4-dichlorophenol and 2,4,6-trichlorophenol are likewise quite soluble in water and do not exhibit a high propensity to adsorb ^{to} in soils.(30) Migratory potential is thus substantial, and if migration occurs, these chlorinated phenols are mobile and persistent. For example, in a damage incident at Montebello, California, involving wastes from 2,4 dichlorophenol manufacture, 2,4-dichlorophenol and other phenolic compounds proved capable of passing through soils and causing longterm pollution of groundwater. (Sinenson, H.A., 1962. The Montebello Incident., Proc. Assoc. Water Treatment and Exam. 11:84-88.) Contamination of groundwater by 2,4-dichlorophenol and other hazardous compounds has also been reported in East St. Louis, Ill. The source of the compounds was the Monsanto chemical dump. (EPA Office of Solid Waste, Hazardous Waste Division, Hazardous Waste Incidents, unpublished, open file 1978.)

Since all of the waste constituents of concern have proven capable of migration, mobility, and environmental persistence, and have in fact caused substantial hazard in actual waste management practice, the Agency believes that the waste constituents could migrate and reach environmental receptors if the wastes are improperly managed. Landfilling the waste without adequate cover could easily result in volatilization of hexachlorobenzene and benzene. Solubilization of hazardous compounds could occur

if rainwater is allowed to percolate through the waste or run off the surface of exposed waste. Waste constituents could then be released if landfills are improperly designed (built without leachate control in areas with permeable soil or located in areas where soils have low attenuative capacity), or managed. Improperly designed wastewater treatment ponds pose the same risk. In the case of improperly managed landfills, surface run-off might also transport compounds that have adsorbed to suspended particulates. Contaminant-bearing leachate and surface run-off may eventually enter ground and surface waters, polluting valuable water supplies and adversely affecting aquatic organisms.

Improper incineration of the distillation residues provides another means by which toxic compounds can be generated and introduced into the environment. If incineration is inadequate (for instance, if temperatures are insufficient or residence time incomplete), inadequate combustion can result in the formation of substances (such as phosgene) that are even more toxic than the original waste.(1) These contaminants can be emitted from the incinerator to the atmosphere and dispersed in the environment.

IV. Health and Ecological Effects

Health and ecological effects and potential transport mechanisms for the constituents of concern that might be found in the distillation bottoms and the separated aqueous waste stream from manufacture of chlorobenzenes are described below:

Benzene

Health Effects Benzene is a human carcinogen. Exposure to benzene as a result of inhalation induces abnormalities in the blood and causes leukemia.(31-3) Benzene administered subcutaneously has been teratogenic in mice at extremely low doses [3 ml/Kg].(34) Chronic inhalation of this chemical in low doses by rats has caused both inhibition and resorption of embryos.(35) Benzene is also mutagenic when administered orally to mice at extremely low doses [1 mg/Kg].(36)

Exposure of humans to benzene has resulted in the reduction of blood cells, impairment of the immunologic system, aplastic anemia and a variety of mutagenic effects in lymphocytes and bone marrow.(37-42) Oral ingestion of benzene in small amounts (50 mg/Kg), or one-seventieth of the oral LD₅₀ in rats, has been lethal in humans.(43)

Regulatory Recognition of Hazard - OSHA has set a revised TLV for benzene at 10 ppm with a maximum permissible exposure of 30 ppm for 10 minutes, within EPA the Offices of Water and Waste Management, and Air Quality Planning and Standards and Toxic Substances are performing a pre-regulatory assessment of benzene based on its environmental effects, high-volume production, spill reports and other health effects. Additionally, benzene has been identified by the Agency as having substantial evidence of being carcinogenic. The Consumer Product Safety Commission requires benzene to carry special labelling.

Industrial Recognition of Hazard - Benzene is designated as highly toxic in handbooks used by industry, such as Plunkett, Handbook of Industrial Toxicology.(44) According to Sax, Dangerous Properties of Industrial Materials(45), benzene represents a fire and moderate exposure hazard.

In addition, benzene is a priority pollutant in accordance with §307 of the Clean Water Act of 1977 and is listed as a hazardous waste or hazardous waste constituent in final or proposed regulations of California, Maine, New Mexico and Oklahoma.

Additional information on the health and ecological effects of benzene may be found in Appendix A.

Chlorobenzenes: Chlorobenzenes are products of the main reaction. Their acute toxic effects are moderate but, because they bioaccumulate to a significant degree, chlorobenzenes may pose a substantial hazard if chronic exposure occurs. They are relatively mobile in the environment and likely to persist for long periods of time.

Chlorobenzene (Monochlorobenzene, MCB)

Health effects - Monochlorobenzene is a central nervous system depressant, with the typical anesthetic effect(46); degeneration of the liver and kidney may develop concurrently with anesthesia produced by this chemical. Acute inhalation of monochlorobenzene has induced narcosis, neuropathy and death in animals during acute inhalation studies.(47) The metabolism of monochlorobenzene may lead to the formation of carcinogenic active

intermediates.(48) Monochlorobenzene is also very bioaccumulative with an octanol/water partition coefficient of 690 (App. B).

Regulatory Recognition of Hazard - The OSHA standard for chlorobenzene is a TWA of 75 ppm. EPA's Office of Water and Waste Management provides technical assistance data and regulation for chlorobenzene under Section 311 of the Clean Water Act. They are also involved with pre-regulatory assessment under the Safe Drinking Water Act. The Office of Air, Radiation and Noise and the Office of Research and Development are involved with pre-regulatory assessment under the Clean Air Act. The Office of Toxic Substances is involved with test rule recommendations under Section 4(e) of the Toxic Substances Control Act.

Monochlorobenzene also is listed as a priority pollutant in accordance with §307 of the Clean Water Act of 1977, and final or proposed regulations of Maine, New Mexico, Oklahoma and California list chlorobenzene as a hazardous waste or a component of hazardous waste. The American Conference of Governmental Industrial Hygienists (ACGIH, 1971) threshold limit value for monochlorobenzene is 350 mg/m^3 .

A more detailed discussion of monochlorobenzene may be found in Appendix A.

Dichlorobenzenes: Ortho- and paradichlorobenzene are products of the main reaction. They are very bioaccumulative, each having an octanol/water partition coefficient of 2500

(Appendix B). A discussion of each isomer follows.

ortho-Dichlorobenzene

Health Effects - Ortho-dichlorobenzene is very toxic in rats [oral LD₅₀ = 500 mg/Kg].(49) Human death has also occurred at this level.(50) Chronic occupational exposure to this chemical and its isomer has resulted in toxicity to the liver, central nervous system and respiratory system.(51) Chronic oral feeding of ortho-dichlorobenzene to rats in small doses has caused anemia as well as liver damage and central nervous system depression.(52)

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 was selected by NCI for Carcinogenesis Bioassay, September 1978. o-dichlorobenzene is listed as a hazardous waste or a component thereof in final or proposed regulations of the States of California, New Mexico and Oklahoma. The Occupational Safety and Health Administration standard and the American Conference of Government Industrial Hygienists threshold values for o-dichlorobenzene is 300 mg/m³. The U.S. EPA draft water quality criterion for total dichlorobenzene is 0.16 mg/l. U.S. EPA has also established criteria for freshwater and marine aquatic life.

para-Dichlorobenzene

Health Effects - Para-dichlorobenzene is very toxic in rats (oral LD₅₀ = 500 mg/kg](53)), having lethal effects in humans ingesting similar amounts.(54) Adverse effects are exerted on the liver and kidney function in humans at a smaller [300 mg/Kg] dose level.(55) This chemical has induced growth depression, liver cell necrosis and death in animals exposed by inhalation.(56)

Regulatory Recognition of Hazard - Para-dichlorobenzene has been designated as a priority pollutant under Section 307(a) of the CWA. p-Dichlorobenzene has an OSHA standard for air TWA of 75 ppm (SCP-T). It is listed as a hazardous waste or a component thereof in final or proposed regulations of the states of California, New Mexico, and Oklahoma. The Occupational Safety and Health Administration Standard and the American Conference of Government Industrial Hygienists threshold values for p-dichlorobenzene is 450 mg/m³. A more detailed discussion of dichlorobenzene can be found in Appendix A.

Tetrachlorobenzene

Health Effects - There is some evidence of liver damage occurring with prolonged exposure of rats and dogs to tetrachlorobenzene. (11,18). Tetrachlorobenzene has an oral rat LD₅₀ of 1500 mg/kg.(14) It is reported to be acutely toxic in varying degrees to some fresh- and saltwater organisms, and chronically toxic to saltwater organisms.(19) The octanol/water partition coefficient for 1,2,4,5-tetrachlorobenzene is extremely high, 47,000.(14) The predominant disposition site for tetrachlorobenzene is suspected to be, or shown to be, in the lipid tissues of the body.(16)

Tetrachlorobenzene is designated by Congress as a priority pollutant under §307 of the Clean Water Act of 1977.

Additional information on the toxic effects of tetrachlorobenzene can be found in Appendix A.

Pentachlorobenzene

Health Effects - Pentachlorobenzene was reported to be carcinogenic in mice, although not in rats or dogs.(21) It was also reported to have caused bone defects in the offspring of rats which had received doses of pentachlorobenzene during gestation.

Pentachlorobenzene is quite acutely toxic at low concentrations (ranging from 160 ug/l to 6,780 ug/l) to both salt- and freshwater organisms, including plants.

Pentachlorobenzene has an extremely high octanol/water partition coefficient of 154,000, indicating a dangerously high bioaccumulation potential.(14)

Pentachlorobenzene is designated as a priority pollutant under §307 of the Clean Water Act.

Additional information on the adverse health effects of pentachlorobenzene can be found in Appendix A.

Hexachlorobenzene

Health Effects - U.S. EPA's Carcinogen Assessment Group (CAG) has evaluated hexachlorobenzene and has found sufficient evidence to indicate that it is carcinogenic. It has also been demonstrated to be fetotoxic to rats.(23) The distribution of hexachlorobenzene is apparently the same in the fetus as in

the adults, with the highest concentration in fatty tissue.

(23) This is expected because of its extremely high octanol/water partition coefficient of 168,000.(14)

Chronic exposure of rats to hexachlorobenzene has caused histological changes in the liver and spleen (24), and in humans, has caused porpyrinuria.(25)

Hexachlorobenzene is designated as a priority pollutant under §307 of the Clean Water Act.

Additional information on the adverse health effects of hexachlorobenzene can be found in Appendix A.

Benzyl Chloride

Health Effects - Benzyl chloride has been identified as a carcinogen(16), and is also mutagenic(27).

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.

Benzyl chloride is listed in Sax's Dangerous Properties of Industrial Materials as highly toxic via inhalation and moderately toxic via the oral route.

Additional information and specific references on the adverse effects of benzyl chloride can be found in Appendix A.

2,4-Dichlorophenol

Health Effects - 2,4-Dichlorophenol is very toxic in rats [oral LD₅₀ = 580 mg/Kg].(61) This chemical is carcinogenic when applied to the skin of mice in small doses.(62) It is also reported to adversely affect cell metabolism.(63,64) An isomer, 2,6-dichlorophenol is also toxic in animals.(65)

2,4-Dichlorophenol has been designated as a priority pollutant under Section 307(a) of the CWA.

Ecological Effects - Small doses of 2,4-dichlorophenol have been lethal to freshwater fish and invertebrates.(66)

Regulations - The Office of Water and Waste Management has completed a pre-regulatory assessment of the proposed water quality criteria under sections 304(a) and 311 of the Clean Water Act. The Office of Research and Development is presently conducting a preregulatory assessment under the Clean Water Act.

Industrial Recognition of Hazard - Sax, Dangerous Properties of Industrial Materials(45), designated a toxic hazard rating of moderate toxicity of 2,4-dichlorophenol. However, chlorinated phenols are designated as highly toxic local and systemic compounds.

Additional information and specific references on the adverse effects of 2,4-dichlorophenol can be found in Appendix A.

2,4,6-Trichlorophenol

Health Effects - 2,4,6-trichlorophenol induced cancer in mice during long-term oral feeding studies.(67) It has also been acutely lethal to humans by ingestion of 60% of the oral

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Ink Formulation

SOLVENT WASHES AND SLUDGES, CAUSTIC WASHES AND SLUDGES AND WATER WASHES AND SLUDGES FROM THE CLEANING OF TUBS AND EQUIPMENT USED IN THE FORMULATION OF INK FROM PIGMENTS, DRIERS, SOAPS AND STABILIZERS CONTAINING CHROMIUM AND LEAD (T).

I. SUMMARY OF BASIS FOR LISTING

Tubs and equipment used in ink formulation are washed by solvents, caustics and/or water. The Administrator has determined that the spent washes and wash sludges generated after ink formulation in which pigments, driers, soaps and stabilizers containing chromium and lead are used 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. The washes and sludges typically contain significant concentrations of lead and chromium. Lead is highly toxic to a variety of species and is reportedly carcinogenic in laboratory animals. Chromium is also toxic and the hexavalent form is a suspected carcinogen.
2. Present management practices may be inadequate to prevent the migration of chromium and lead from a disposal site. Disposal practices subject to RCRA include landfilling, impoundment and removal by contract haulers. Such practices, if uncontrolled, can result in contamination of ground and surface waters by lead and chromium.

II. INDUSTRY DESCRIPTION AND MANUFACTURING PROCESS(1)

An EPA survey of the ink formulating industry indicates that there are approximately 460 ink manufacturers in the United States (excluding captive ink producers that manufacture ink in a printing plant solely for use in that plant). The

distribution of ink manufacturing plants by state is given in Table 1. In 1972, total ink production was greater than one billion pounds.

The variety of inks used today is broad, ranging from ordinary writing inks to specialized magnetic inks. Inks manufactured for the printing industry, which utilizes a major portion of ink production, fall into four major categories: letterpress inks, lithographic inks, flexographic inks, and gravure inks.

Letterpress inks are viscous, tacky pastes using vehicles that are oil and varnish-based. They generally contain resins and dry by the oxidation of the vehicle.

Lithographic or off-set inks are viscous inks with a varnish-based vehicle, similar to the letterpress varnishes. The pigment content is higher in lithographic inks than letterpress ink because the ink is applied in thinner films.

Flexographic inks are liquid inks which dry by evaporation, absorption into the substrate, and decomposition. There are two main types of flexographic inks: water and solvent. Water inks are used on absorbent paper and the solvent inks are used on nonabsorbent surfaces.

Gravure inks are liquid inks which dry by solvent evaporation. The inks have a variety of uses ranging from printing publications to food package printing.

Inks are either water, oil or solvent-based. The "average" plant produces approximately 60 percent oil base

Table 1 (1)

DISTRIBUTION OF INK MANUFACTURING PLANTS BY STATE

State	Number of Plants	Percent of Plants
California	47	10.2
Illinois	46	10.0
New Jersey	39	8.5
New York	34	7.4
Ohio	28	6.1
Pennsylvania	24	5.2
Texas	22	4.8
Massachusetts	21	4.6
Georgia	20	4.3
Missouri	16	3.5
Florida	14	3.0
Wisconsin	14	3.0
Michigan	13	2.8
Tennessee	13	2.8
North Carolina	10	2.2
Louisiana	9	2.0
Maryland	9	2.0
Minnesota	9	2.0
Virginia	9	2.0
Indiana	7	1.5
Oregon	7	1.5
All Others	49	10.7

ink, 25 percent solvent base ink and 5 percent water base ink.

In the manufacture of inks, the major ingredients (vehicles, pigments and driers) are mixed thoroughly to form an even dispersion of pigments within the vehicle.

The mixing is accomplished with the use of high-speed mixers, ball mills, three-roll mills, sand mills, shot mills, and/or colloid mills.

Most inks are made in a batch process in tubs ranging in sizes from 19 liters (five gallons) to over 3,750 liters (1,000 gallons). The number of steps needed to complete the manufacture of the ink depends upon the dispersion characteristics of the ingredients. Most inks can be completely manufactured in one or two steps since many of the pigments used can be obtained predispersed in a paste or wetted form.

III. GENERATION AND MANAGEMENT OF HAZARDOUS WASTE⁽¹⁾

Ink is manufactured by blending raw materials; chemical reactions generally do not occur and no by-products are formed. When required, production tubs and manufacturing equipment are washed clean of residue or clingage from the formulation process. The spent cleaning solutions become impregnated with tank residue composed of the residual raw materials.

There are four broad types of raw materials used in ink manufacture:

- ° Pigments and Dyes, Flushes and Dispersions
- ° Chemical Specialties (including driers, plasticizers, soaps and stabilizers)
- ° Resins
- ° Solvents

Inorganic pigments are the primary source of chromium and lead in ink industry wastewaters, although chemical specialties are also reported to contain lead. Survey data obtained by EPA show that the ink formulation industry relies on inorganic pigments for about 40% of the total production. The two most widely used lead and chromium-containing pigments are chrome yellow and molybdate orange, although many other pigments are sources of lead and chromium in the waste.

Particular chemical specialties are another significant source of lead and chromium in these wastes. For example, driers containing lead are used by approximately 30% of the industry.* Stabilizers containing lead and phenol, and metallic soaps and flatting agents containing lead are also in use and are expected to contribute significant concentrations of lead to process wastes.**

* Examples are Shephard-Lead Tallates, Lead Linoleates, Hexogan, Aduasol and Catalox.(1)

**Industry survey data indicate that approximately 70% of the manufacturers use chromium-containing raw materials, and 55% use lead-containing raw materials. Thus, use of materials containing these pollutants is widespread in the industry.

The ink industry commonly uses three methods of ink tub cleaning: (1) Solvent-wash; (2) Caustic-wash; and (3) Water-wash.

(1) Solvent-Wash Wastes

Solvent-wash is used exclusively to clean tubs used for formulating solvent-based and oil-based ink. The dirty solvent generally is handled in one of three ways:

1. used in the next compatible batch of ink as part of the vehicle;
2. collected and redistilled, either by the plant or by an outside contractor for subsequent resale or reuse; or
3. reused with or without settling to clean tubs and equipment until spent, and then drummed for disposal. If sludge is settled out it is also drummed. These spent solutions and sludges are usually disposed of by contract hauling.

(2) Wash-Water Wastes

Water-washing techniques are used in both the solvent-base and water-base segments of the ink industry. For solvent-base operations, water-washing usually follows caustic washing of solvent-base tanks. For water-base operations, water washes often constitute the only tub cleaning operation, although water-base ink tubs may be cleaned periodically with caustic.

Wastewater generated by rinsing tubs or equipment used for manufacturing water-base ink is usually handled in one of four ways:

1. reused in the next compatible batch of water-base ink as part of the vehicle;

2. reused either with or without treatment to clean tubs and equipment until spent and disposed. If sludge is settled out it is disposed by contract hauling;
3. discharged with or without treatment as wastewater; or
4. disposed of immediately by contract hauling.

The water rinse following a caustic-wash is rarely reused in a subsequent batch of ink. The most common methods for disposal of this rinse are:

1. recycling it back into the caustic as make-up water;
2. drumming it for contract hauling;
3. discharging it as wastewater, with or without pre-treatment. Combination with other wastewater prior to treatment or disposal is sometimes practiced. Discharge of this wastewater is currently prohibited by some states and municipalities and may be prohibited in other areas in the future.

(3) Caustic-Wash Wastes

Caustic wash techniques are used to clean both solvent-base and water-base ink manufacturing tanks. Plants using caustic rinse or washing systems usually rinse the caustic residue with water, although a few plants allow the caustic solution to evaporate in the tubs. There are several types of caustic systems commonly used by the ink industry. For periodic cleaning of fixed tubs two methods are popular:

1. maintaining the caustic in a holding tank (usually heated) and pumping through fixed piping or flexible hose to the tub to be cleaned. After cleaning, the caustic is returned to the holding tank; and
2. preparing the caustic solution in the tub to be cleaned, and soaking the tub until clean. The caustic solution is either transferred to the next tub to be cleaned, stored in drums or a tank for subsequent use, or is discarded.

For cleaning small portable tubs, three common methods are used by the ink industry:

1. pumping caustic from a holding tank (usually heated) to nozzles in a fixed or portable hood which is placed over the tub to be cleaned. The caustic drains to a floor drain or sump and is pumped back to the tank, or is pumped back directly from the tub;
2. maintaining an open top caustic holding tank. Small tubs are put into "strainers" and dipped into these tanks until clean; and
3. placing the tubs in a "dishwasher-like" device (which circulates hot caustic), and a subsequent water rinse. These devices can handle tubs up to about 1900 liters (500 gal).

Most plants using caustic recycle the caustic solution until it loses some of its cleaning ability. The spent caustic is then disposed of either by contract hauling or as a wastewater, with or without neutralization or other treatment.

The most common methods of wastewater disposal are discharge to a sewer, contract hauling, evaporation, and landfill or impoundment. Most contract haulers discharge the sludge to a landfill, although a few incinerate or reclaim it.

Although precise figures on the amount of waste covered by this listing are not available, the quantity is expected to be significant, and, furthermore, is expected to increase in the future. Final regulations issued by EPA's Effluent Guidelines Division impose zero discharge requirements for certain pollutants on all ink manufacturers in the solvent wash category of the industry except existing

pre-treaters; proposed regulations would impose zero discharge requirements on existing pre-treaters in the Solvent Wash category and all others in the Caustic and/or Water Wash category. Implementation of these regulations will increase the amount of hazardous waste requiring disposal in accordance with the RCRA Subtitle C regulations.

V. DISCUSSION OF BASIS FOR LISTING

A. HAZARDS POSED BY THE WASTE

Solvent washes and sludges, caustic washes and sludges and water washes and sludges from cleaning equipment used in the formulation of ink from raw materials containing chromium and lead are listed as hazardous because they typically contain significant concentrations of lead and chromium.* Lead is poisonous in all forms. It is one of the May 19, 1980 (45 FR 33063), and if these solvents are used in ink formulation and are disposed of, they are considered hazardous wastes under the earlier listing as well as the most hazardous of the toxic metals because it accumulated in

* Other toxic heavy metals and various toxic organics are also known to be present in some of the wash wastes, but sufficient data are not yet available to list the wastes for those contaminants. It also should be noted that the tub-cleaning wastes can exhibit hazardous characteristics other than toxicity; the Agency has information which indicates that the listed wastes can be ignitable or corrosive (3,4,5,6). In addition, a number of spent solvents are listed as hazardous in §261.31 of the hazardous waste regulations published May 19, 1980 (45 FR 33063), and if these solvents are used in ink formulation and are disposed of, they are considered hazardous wastes under the earlier listing as well as the present listing. Listed solvents presently in use by the ink formulation industry are: toluene, 1,1,1-trichloroethane, carbon tetrachloride, methylene chloride and trichloroethylene⁽¹⁾. Delisting petitions by ink formulators using these solvents must address not only the presence of the spent solvent itself in the waste, but the presence of lead and chromium as well.

many organisms and its deleterious effects are numerous and severe. Epidemiology studies implicate occupational exposure to chromium in the induction of lung tumors. Impairment of pulmonary function is also reported to result from chronic exposure to chromium. (For further information on Health and Ecological Effects of Chromium and Lead, see Appendix A.)*

The following data substantiate the presence of significant concentrations of lead and chromium in the wash wastes:

- ° EPA has determined that the average concentrations of lead and chromium per day in ink industry caustic wash and water-wash wastewaters are 151 mg/l and 35 mg/l, respectively. Concentrations as high as 900 mg/l of lead and 200 mg/l of chromium were reported.(1)**
- ° A summary of industrial waste composition data taken from the manifests required by the State of California for transportation of hazardous wastes lists the following wastes from the manufacture of printing ink as hazardous:(2)
 1. Ink wastewater which contained 1000 ppm of lead.
 2. Equipment cleaning washwater which contained 10,000-20,000 ppm of lead chromate.
- ° "Special Waste Disposal Applications" were submitted to the State of Illinois for the following wastes from ink manufacture:(3)
 1. Solvent waste containing 120 ppm of chromium and 770 ppm of lead.
 2. Solvent waste containing 291 ppm of lead.
- ° A "Hazardous Waste Disposal Request" was submitted to the Missouri Department of Natural Resources for disposal of printing ink sludge (wash waste) containing 260 ppm of chromium and 1,340 ppm of lead.(4)
- ° The "Industrial Waste Surveys" file of the State of New Jersey contained a description of ink manufacturing wash water with 260 ppm of lead (7).

*It should be noted that even if chromium migrates in the trivalent form, it is capable of oxidation to the far more dangerous form under normal environmental conditions. See Background Document for Extraction Procedure Toxicity Characteristic at pp. 109-112.

**These figures may be conservative in light of the higher concentrations contained in state manifests, given below.

Clearly the concentrations of lead and chromium in the wastes may be very substantial.

The presence of such high concentrations of toxic metals in a waste in and of itself raises regulatory concerns. Lead and chromium have proven capable of migration, mobility and persistence in many waste management settings(28), raising the concern that, if these wastes are improperly managed, the lead and chromium may be released from the waste in harmful concentrations and adversely effect human health and the environment. Because lead and chromium do not degrade with the passage of time, they will provide a potential source of long-term contamination if they are permitted to escape from the disposal site.

Current disposal methods do not appear adequate to prevent migration of these toxic heavy metals from the waste into the environment. Toxic metal-bearing liquid wastes placed in an impoundment can release those hazardous constituents to the surrounding area if seepage and overflow are not controlled, or measures are not taken to prevent total washout. Without regulation, proper containment of the impounded wash wastes cannot be assured.

Clearly, if measures to retard migration of liquids from impoundments and landfills are not employed, ground and surface waters could easily become contaminated. Improper landfilling of sludges settled from the liquid wastes could also result in release of the hazardous constituents. The

heavy metal compound might already be solubilized or may solubilize as a result of disposal conditions (co-disposal with acids, alkalis or decomposing organic matter, for instance) and could then migrate from the disposal site to ground and surface waters. As a result, ground and surface drinking water supplies may become contaminated, and the existence of wildlife and various aquatic species could be threatened by exposure to the toxic heavy metals.

Unregulated contract hauling of wastes by private disposal services, scavengers or purveyors in tank trucks -- a waste management method frequently used for these wastes -- creates additional hazards. There have been innumerable damage incidents involving unregulated contract hauling, resulting in substantial environmental harm. (Some examples are collected in Reference 28.) Thirty-one percent of the ink plants surveyed by EPA did not know what the contract hauler does with their waste.⁽¹⁾ There is obvious potential for abuse in this system since there is no way to determine whether these wastes are properly managed during transportation, treatment or disposal; irresponsible handling at any point could ultimately endanger human health and the environment. Therefore, it is essential that wastes of this nature be subject to regulation from "cradle to grave".

B. Health and Ecological Effects

1. Lead

Health Effects

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. The hematopoietic system is the most sensitive target organ for lead in humans, although subtle neurobehavioral effects are suspected in children at similar levels of exposure.(8)

Lead exposure has been reported to decrease reproductive ability in men(9) and women.(10) It has also been shown to cause disturbances of blood chemistry,(11) neurological disorders,(12,13), kidney damage(14) and adverse cardiovascular effects.(15) Lead has been shown to be teratogenic in animals.(16) Although certain inorganic lead compounds are carcinogenic to some species of experimental animals, a clear association between lead exposure and cancer development has not been shown in human populations.

Additional information and specific references on adverse effects of lead can be found in Appendix A.

Ecological Effects

In the aquatic environment, lead has been reported to be acutely toxic to invertebrates at concentrations as low as 450 ug/l and chronically toxic at less than 100 ug/l.(17) The comparable figures for vertebrates are 900 ug/l for acute toxicity(18) and 7.6 ug/l for chronic toxicity.(19) Lead is bioconcentrated by all species tested - both marine and freshwater - including fish, invertebrates and algae.

The mussel, Mytilus edulis, concentrated lead 2,568 times that found in ambient water. Two species of algae concentrated lead 900-1000 fold. Algae reportedly can concentrate lead in their tissues to levels as much as 31,000 times ambient water concentrations.(20) Lead does not degrade with the passage of time and may be expected to persist indefinitely in the environment in some form.

Regulatory Recognition of Hazard

As of February 1979, the U.S. Occupational Safety and Health Administration has set the permissible occupational exposure limit for lead and inorganic lead compounds at 0.05 mg/m³ of air as an 8-hour time-weighted average. The U.S. EPA (1979) has also established an ambient airborne lead standard of 1.5 ug/m³.

The U.S. EPA has derived a draft criterion for lead of 50 ug/l for ambient water.(21) This draft criterion is based on empirical observation of blood lead in human population groups consuming their normal amount of food and water daily.

In addition, final or proposed regulations of the States of California, Maine, Massachusettes, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define lead containing compounds as hazardous wastes or components thereof.(22)

Industrial Recognition of Hazard

Lead is rated as highly toxic through ingestion, inhalation and skin absorption routes in Sax, Dangerous Properties of Industrial Materials.

Chromium

Health Effects

Hexavalent chromium is an animal carcinogen and there is some evidence that it may be a human carcinogen as well.(23) EPA's Carcinogen Assessment Group has listed it as such. Mutagenic effects in bacteria have been described. Cytogenetic effects in workers using hexavalent chromium compounds have been reported.(24)

Teratogenic effects of chromium have been reported in a single study and have not been confirmed.

Impairment of pulmonary function has been described in chrome electroplating workers subject to chronic chromium exposure.(25)

Additional information and specific references on the adverse effects of chromium can be found in Appendix A.

Ecological Effects

Hexavalent chromium, at low concentrations, is toxic to many aquatic species. For the most sensitive aquatic species, Daphnia magna, a final chronic no-effect level of less than 10 ug/l has been derived by the U.S. EPA. For trivalent chromium, toxic effects are more pronounced in soft than in hard water.(26)

Regulatory Recognition of Hazard

Based on animal data indicating carcinogenic effects of chromium VI and estimates of lifetime exposures from consumption of both drinking water and aquatic life forms, the U.S.

EPA(27) has estimated levels of hexavalent chromium in ambient water which will result in specified risk levels of human cancer:

<u>Exposure Assumptions (per day)</u>	<u>Risk Levels and Corresponding Criteria</u>			
	<u>0</u>	<u>10^{-7}</u>	<u>10^{-6}</u>	<u>10^{-5}</u>
2 liters of drinking water and consumption of 18.7 grams fish and shellfish	0	0.08 ng/l	0.8 ng/l	8 ng/l
Consumption of fish and shell fish alone	0	8.63 ng/l	86.3 ng/l	863 ng/l

The OSHA time-weighted average exposure criterion for chromium (carcinogenic compounds) is 1 ug/m^3 ; for the "non-carcinogenic" classification of chromium compounds the criterion is $25 \text{ ug/}^3 \text{ TWA}$.

For the protection of aquatic species, proposed water criteria for both trivalent and hexavalent chromium in fresh-water and marine environments have been prepared in accordance with the Guidelines for Deriving Water Quality Criteria.(27)

Industrial Recognition of Hazard

Sax, Dangerous Properties of Industrial Materials, 4th Ed. 1975, rates chromium as having a high pulmonary toxicity.

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Comments

The National Association of Printing Ink Manufacturers (NAPIM) commented that the proposed listing is too broad and that all wash wastes should not be considered hazardous.

The listing of the above waste has been clarified.

After reviewing available information, the Agency has narrowed the listing to cover waste wastes from tub in which ink is formulated from raw materials containing chromium and lead. Data show that chromium and lead containing raw materials are widely used in the industry, and the wash wastes generated when these raw materials are used are likely to exhibit substantial concentrations of the toxic metals. The Agency concluded that these wash wastes present a potential hazard to human health and the environment because improper disposal may result in the contamination of ground and surface waters used as drinking water sources (see the background document for a more detailed discussion).

The NAPIM comments stated that wash wastes should not be listed as corrosive since the corrosive waste streams can be neutralized.

The fact that the wastes can be neutralized does not mean that they are not hazardous when generated. In order to make sure that corrosive wastes are managed properly, corrosivity must be determined before treatment by neutralization or any other means (see §261.3(b)(3)).

For the final listing, the Agency has decided not to characterize the wash wastes as corrosive because adequate data are not available to indicate that the wastes are typically corrosive as defined in §261.22. In addition, the Agency believes that the corrosivity of the wastes can easily be determined by the generator. Such a determination is, of course, required for all wastes not included in this listing, and for all wastes addressed by individual petitions for delisting. (See §§ 262.11, 260.22.)

NAPIM stated that classification of all wash wastes as hazardous because some might contain toxic organic substances is arbitrary.

The Agency has narrowed its proposed listing, although the unsubstantiated comments submitted by NAPIM are not particularly persuasive. The revised listing does not address toxic organic substances in the waste and may be changed shortly to include ink formulation wastes containing organic contaminants. In this regard, the Agency is particularly concerned with the use of phthalates in plasticizers used in ink formulation, and use of phenols in chemical specialties. Information is solicited as to concentrations of these materials in ink formulation wastes, and potential mass loadings of these pollutants. As mentioned previously, certain spent solvents are already listed as hazardous wastes due to their toxicity.

Veterinary Pharmaceuticals

LISTING BACKGROUND DOCUMENT

Wastewater treatment sludges generated during the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds (T).

Residue from the use of activated carbon for decolorization in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds (T) (proposed)*/

Distillation tar residues from distillation of aniline-based compounds in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds (T) (proposed)*/

I. SUMMARY OF BASIS FOR LISTING

Treatment of wastewater from the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds generates a wastewater treatment sludge containing arsenic or organo-arsenic compounds. The production of this class of veterinary pharmaceuticals likewise generates other arsenic-containing wastes, proposed for listing in this document.

The Administrator has determined that these wastewater treatment sludges and other arsenic-containing wastes from the production of veterinary pharmaceuticals 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:

*/These waste streams were not included in the initial listing, and are being initially proposed in the present document.

1) These wastes have been shown to contain high concentrations of arsenic. Arsenic is highly toxic and has been identified by the Agency as a substance which has demonstrated substantial evidence of being carcinogenic. It has also been shown to be mutagenic to bacteria and teratogenic to laboratory animals.

2) Disposal of these wastes in improperly designed or operated landfills has resulted in arsenic contamination of ground and surface water, providing empirical proof that the arsenic in this waste is soluble and may migrate from disposal sites into soil, groundwater and surface water in concentrations sufficient to create a substantial hazard. Further, since arsenic persists in the environment, any contamination caused by mismanagement of these wastes will be long-term.

3) These wastes are generated in large quantities, so that large amounts of arsenic are potentially available for environmental release, an additional hazard posed by this waste.

II. SOURCES OF THE WASTE AND TYPICAL DISPOSAL PRACTICES

A. Profile of the Industry

Three companies produce veterinary pharmaceuticals containing arsenic: Salsbury Laboratories in Charles City, Iowa; Whitmoyer Laboratories in Meyerstown, Pennsylvania; and Fleming Laboratories in Charlotte, North Carolina.(1,2)

B. Manufacturing Process and Waste Generation

Manufacture of arsenic-containing pharmaceuticals requires the reaction of an organic compound with inorganic arsenic to form the organic arsenical product. Arsenic-containing solid wastes generated during the production process include tars from the distillation of aniline-based compounds, and residue from the use of activated carbon in the decolorization of pharmaceuticals.(4) Whitmoyer

reported that it generates these wastes in annual quantities of 100 55-gallon drums and 630 55-gallon drums, respectively.(4) Salsbury Labs also generates arsenic-containing tars from production processes.(5)

Production of veterinary pharmaceuticals from arsenic compounds generates wastewaters which contain organic and inorganic arsenic. Treatment of these wastewaters produce arsenic-bearing sludges. Figure 1 summarizes the wastewater treatment system at Salsbury Laboratories, which produces organic arsenicals marketed as feed additives for chickens, turkey and swine.(1) Process wastewaters at Salsbury are segregated into two sewer systems, of which only the second generates a listed hazardous waste. As a point of clarification, the first sewer system (the source of a non-listed waste) carries waste acid washwater (10,000 gallons per day) from the nitration processes; this washwater is neutralized and clarified. These solids are not believed to contain arsenic, and are not listed in this document.*/

The second sewer system --the source of the listed waste-- collects approximately 25,000 to 30,000 gallons per day of arsenic-containing process wastewaters which originate from

*/Generators must still determine, however, whether this waste stream meets any of the characteristics of hazardous waste contained in §§261.21-24 of the regulations.

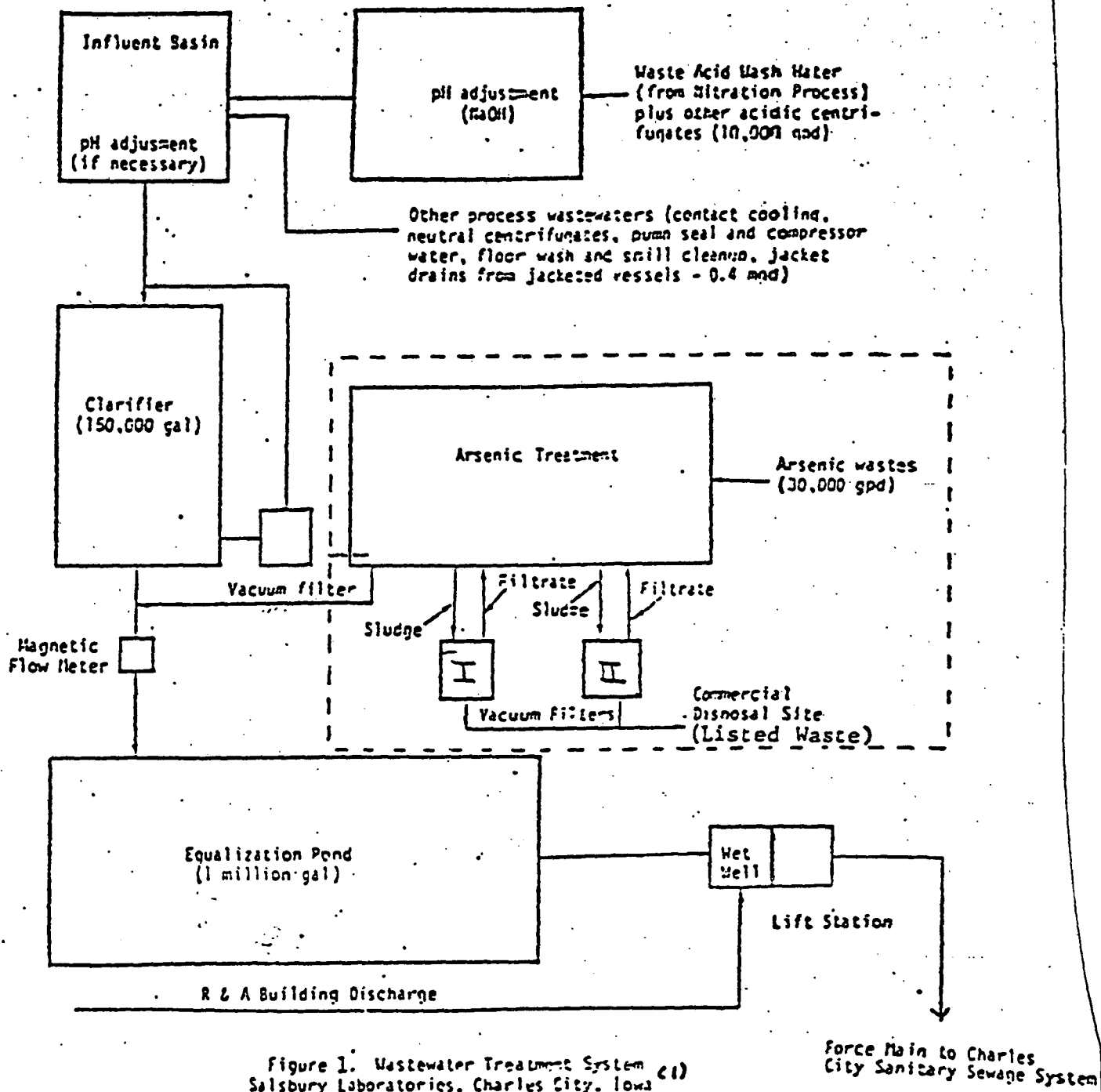


Figure 1. Wastewater Treatment System (1)
Salisbury Laboratories, Charles City, Iowa

the manufacture of Salsbury's arsenical compounds, 3-nitro-4-hydroxyphenylarsonic acid and 4-nitrophenylarsonic acid. The waste treatment process, indicated in Figure 1 by a dashed line, is operated on a batch basis and consists of two parallel systems of treatment basins. The first set of treatment basins works within the box marked "arsenic treatment"; the second set of treatment basins works within the two vacuum filter boxes located below the arsenic treatment box in Figure 1. During "arsenic treatment", slaked lime and a flocculating agent are added to each batch, resulting in pH adjustment to 11.2 - 11.4, and subsequent precipitation of inorganic arsenic. The supernatant liquor is decanted and the precipitate [$\text{Ca}_3(\text{AsO}_4)_2$ and $\text{Ca}_3(\text{AsO}_3)_2$] is filtered (vacuum filter box I, Figure 1) on a pre-coated rotary drum vacuum filter. The filtrate and decant liquors are combined and re-introduced into the arsenic treatment box for treatment with MnSO_4 and a flocculating agent. The pH is lowered to 7.0 with HCl or H_2SO_4 to form a precipitate which is then drawn off to the second pre-coated rotary drum vacuum filter (filter box II, Figure 1). The filtrate and decant liquors are mixed with clarifier overflow, which presumably contains no arsenic.

The remaining manufacturers of arsenic-containing veterinary pharmaceuticals also produce arsenic sludges. Whitmoyer Laboratories generates approximately 1,260 drums per year of sludge from the evaporation, volume reduction

and centrifugation of waste salt solutions.(4) Fleming Laboratories reported the production of arsenic sludges, but did not describe the process by which they are generated (24).

The wastewater treatment sludges are believed to contain large amounts of arsenic. A sample of fresh sludge from the Salsbury Laboratories disposal site, the LaBounty landfill, contained 28,000 ppm of arsenic. In addition, the fact that significant concentrations have been released from the waste at the LaBounty site indicates that the contaminant is present in substantial amounts thus, borings from underlying soils exhibited a mean arsenic concentration of 700 ppm and borings from surrounding soils exhibited a mean concentration of 2200 ppm. Samples obtained from a well located between the site and the river showed an arsenic concentration of 590 ppm in groundwater.(1) That these sludges typically contain a large quantity of the contaminant is further supported by a report that Whitmoyer's sludges contain 1-7% arsenic.(4)

Arsenic concentrations in the other listed wastes are also substantial; distillation tars are reported to contain 10-15% arsenic, and residues from activated carbon decolorization contain 4-14% arsenic.(4)

C. Waste Management

From 1953 to December, 1977, Salsbury Laboratories disposed of its solid wastes in the LaBounty Dump, located on the west bank of the Cedar River. (1) Prior to 1953,

solid wastes were disposed of across the river at the municipal dump, but quantities are estimated to be relatively minor compared to those at the LaBounty site. The wastewater treatment sludge presently is stored in drums and shipped by rail to Waste Management, Inc., a commercial disposal operation in Livingston, Alabama.(3)

Whitmoyer Laboratories' treatment sludges were stored in on-site lagoons until groundwater contamination was detected (this was also the disposal practice under prior ownership). Off-site disposal has been utilized since that time. Since 1975, Whitmoyer Laboratories has drummed all of its arsenic-containing wastes, and has shipped these wastes to landfills specially designed to impede release of hazardous constituents to the environment.(4)

III. DISCUSSION OF BASIS FOR LISTING

A. Hazards Posed by the Waste

These treatment sludges, distillation tars, and activated carbon residues contain high concentrations of arsenic, an extremely toxic substance. Arsenic and arsenic compounds have been identified by the Agency as a substance which has demonstrated substantial evidence of carcinogenicity. Arsenic is mutagenic to bacteria and teratogenic to laboratory animals. See Appendix A for further information.

It is quite obvious that improper management of these wastes can result in substantial hazard, since substantial harm has in fact occurred from their faulty management. The

most notorious example of this damage caused by mismanagement of this waste at the LaBounty landfill.

Various wastes, including large amounts of arsenic sludges, were disposed of at the LaBounty site. In January, 1978 approximately 7.5 cubic meters of arsenic sludge were disposed per day. (1) At one time it was estimated that the site contained more than six million pounds of arsenic(1). The site is located over a major aquifer. As noted above, substantial arsenic contamination of soil and groundwater resulted when the arsenic compounds leached from the waste site. As a result of surface run-off and groundwater discharge, the Cedar River picked up an average load of 53 kg of arsenic per day in the vicinity of the LaBounty Site.(1) The Iowa Department of Environmental Quality issued an order that required Salsbury to cease disposal of wastes at the LaBounty landfill. (77-DQ-01, Dec. 14, 1977).

A report on this damage incident concluded that arsenic in the wastewater treatment sludge is "fairly easily solubilized even if it is precipitated with calcium as the arsenate ($\text{Ca}_3(\text{AsO}_4)_2$)".(5) The presence of arsenic in ground and surface waters in the vicinity of the LaBounty Site likewise clearly indicates that, once released from the waste, it is highly mobile and persistent.

The migratory potential of the arsenic contained in these wastes is also substantiated by the groundwater

contamination resulting from the storage of the listed waste and similar wastes by Whitmoyer Laboratories in holding lagoons (4). When the groundwater contamination was discovered in the late 1960's, the company began disposing of the sludges at a number of different sites; presently, these wastes are transported by truck to hazardous waste landfills or a specially designed vault disposal operation (4). Again, this demonstrates the potential hazard posed by the migration of waste constituents from a disposal site and the generator's subsequent recognition of this hazard.

An additional demonstration of the necessity for proper management occurred when Salsbury Laboratories, as a result of a cease order, began disposing of solid wastes in a temporary on-site holding basin.(1) This disposal method was quickly terminated because leachate was detected in the underdrain system within 24-hours after disposal.(1) The 1977 court action, coupled with the present management of these wastes in chemical waste landfills, substantiates the concern by both the state and the generator for the proper management and disposal of this hazardous waste.

These damage incidents show that arsenic may easily migrate from these wastes and persist in the environment upon release. Indeed, because arsenic is an element, and does not degrade with the passage of time, it will persist in some form virtually indefinitely.

There are a number of additional reasons to impose hazardous waste status on this waste. Unregulated transpor-

tation of this waste to off-site disposal facilities also increases the likelihood of harmful exposure to human beings and the environment. Without proper means to track the waste from the point of generation to its ultimate destination, the waste might not reach its designated destination at all, thus making it available to do harm elsewhere.

Furthermore, as previously indicated, arsenic sludges from the production of veterinary pharmaceuticals are generated in very substantial quantities (in January 1978, approximately 7.5 m³/day at Salisbury plant (1)). Large amounts of arsenic are thus available for potential environmental release. The large quantities of this contaminant 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 this pollutant are available for environmental loading. Attenuative capacity of the environment surrounding the disposal facility could also be reduced or exhausted due to the large quantities of pollutant available. All of these considerations increase the possibility of exposure to this harmful constituent.

B. Health and Ecological Effects

Health Effects

Arsenic is very acutely toxic to animals and humans (6). Death in humans has occurred following ingestion of very small amounts (5mg/kg) (7). Several epidemiological studies have associated cancers with occupational exposure

to arsenic (8-10), including those of the lung, lymphatics and blood (11,12). Skin cancer has been associated with the presence of arsenic in drinking water (13), while liver cancer has developed in several cases following ingestion of arsenic (14). The human carcinogenic potential of arsenic is supported by animal studies.

Occupational exposure to arsenic has also resulted in chromosomal damage (15), and several different arsenic compounds have demonstrated positive mutagenic effects in laboratory studies (16-18). The teratogenicity of arsenic and arsenic compounds is well established (19-21); observed defects include those of the skull, brain, kidneys, gonads, eyes, ribs and genitourinary system.

The effects of chronic arsenic exposure include skin diseases progressing to gangrene, liver damage, neurological disturbances (22), disturbances in red blood cell production and cardiovascular disease (8).

Additional information and specific reference on 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; concentrations as low as 128 ug/l are acutely toxic to freshwater fish. Based on one chronic life cycle test using Daphnia magna, a chronic value for arsenic was estimated at 853 ug/l (21).

Regulatory Recognition of Hazard

OSHA has set a standard 8-hr air TWA in air of 0.5 mg/m^3 for occupational arsenic exposure. 0.05 mg/m^3 has been proposed for arsenic trioxide (23). DOT requires a "poison" warning label.

EPA's Office of Toxic Substances under FIFRA has issued a pre-RPAR. The Carcinogen Assessment Group has identified arsenic and its compounds as a substance which has demonstrated substantial evidence of being carcinogenic. Arsenic is designated as a priority pollutant under Section 307(a) of the CWA. The Office of Drinking Water has regulated arsenic under the Safe Drinking Water Act 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 oncogenicity and environmental effects. Finally, the Office of Toxic Substances has completed Phase I assessment of arsenic under the Toxic Substances Control Act.

Industrial Recognition of Hazard

Arsenic is rated as highly toxic through intra-muscular and subcutaneous route in Sax, Dangerous Properties of Industrial Materials (22). Arsenic is rated as highly toxic through ingestion, inhalation, and percutaneous routes in

Patty, Industrial Hygiene and Toxicology.

A ten-fold reduction (to 0-.05 mg/m³) of the present OSHA standard for arsenic trioxide has been proposed (23).

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Coking

LISTING BACKGROUND DOCUMENT

COKING

Decanter Tank Tar-Sludge*(T)

I. Summary of Basis for Listing

The spray cooling of coke oven gases during the by-product recovery process results in the generation of a decanter tank tar-sludge. The Administrator has determined that decanter tank tar-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) The tank tar-sludge contains significant concentrations of phenol and naphthalene. Phenol is highly toxic, and an animal carcinogen. Naphthalene is also toxic and is a demonstrated neoplastic substance in experiments done on laboratory animals.

2) Phenol has leached in significant concentration from a waste sample tested in a distilled water extraction procedure. Although no leachate data is currently available for naphthalene, the Agency believes that, due to its presence in the tar in high concentrations and due to its relative solubility, naphthalene also may leach from the waste in harmful concentrations if the waste is improperly managed.

3) These tar-sludges are often land disposed in on-site landfills or dumped in the open. These methods may be inadequate to impede leachate migration and resulting groundwater contamination.

*The listing description has been amended from that originally proposed on December 18, 1978 (43 FR 58959) which included two waste listings [i.e., Coking: Decanter tank tar and Coking: Decanter tank pitch/sludge]

II. Waste Generation, Composition and Management

Coke, the residue from the destructive distillation of coal, serves as both a fuel and as a reducing agent in the making of iron and steel. Some coke plants recover by-products given off or created during the coke production process, and the recovery of by-products generates the sludge which is listed in this document. There are 66 by-product coke plants, which generate an estimated 72,300 tons/yr of decanter tank tar-sludge. During the recovery of chemicals in the by-product coke production process, tar separates by condensation from coke oven gas and drains to a decanter tank. Recoverable oil fractions are decanted off the top and the tar sludge settles to the bottom.

Approximately 97% of this tar-sludge is elemental carbon. The remaining 3% consists of condensed tar materials. These condensed tar materials contain the waste constituents of concern, namely phenolic compounds and naphthalene, which are formed as a result of the destructive distillation of coal.

Based on a published reference, the condensed tar component contains, by weight, 2.2% naphthalene and 0.1% phenolic compounds⁽²⁾. With an estimated 2,169 tons/yr of condensed tar contained in the amount of tar-sludge generated annually (i.e., 3% of the 72,300 tons/yr of tar-sludge), approximately 47.7 tons of naphthalene and 2.2 tons of phenolic compounds will be contained in the waste generated each year^(1,2).

Of the 66 coke plants generating decanter tank tar-sludge, 30 plants use the tar-sludge as a raw material in either the sintering process or open hearth furnace operation. The remaining 36 plants dispose of this waste in unsecure on-site landfills⁽¹⁾, or by dumping in the open⁽³⁾.

III. Hazardous Properties of the Waste

Phenol and naphthalene are present in the tar component of this waste in significant concentrations: 0.1% by weight (1000 ppm) and 2.2% by weight (22,000 ppm), respectively⁽²⁾. Phenol is highly toxic and is also an animal carcinogen, while naphthalene is toxic. Thus, the Agency believes that the concentrations of these materials in the waste are quite significant, in light of the constituents' known health hazards. Further, these waste constituents appear capable of migrating in significant concentrations if mismanaged, and are likely to be mobile and persistent so that waste mismanagement could result in a substantial human health or environmental hazard.

Phenol's potential for migration from this waste in significant concentrations has been demonstrated empirically. Phenol leached in significant concentration (approximately 500 ppm) from a decanter tar-sludge waste sample subjected to distilled water extraction procedure.⁽³⁾ In addition, phenol is extremely soluble, about 67,000 ppm @ 25°C⁽⁵⁾, indicating high potential for migration. Phenol biodegrades at a moderate rate in surface water and soil but moves very

readily (App. B). Even with a persistence of only a few day, the rapid spreading of phenol could cause widespread contamination of the eco-system and contamination of potable water supplies.

The migratory potential of phenol and its ability to move through soils is further confirmed by the fact that it has been detected migrating from Hooker Corporation's S Area, Hyde Park, and 102nd St. landfills in Niagara, New York (OSW Hazardous Waste Division, Hazardous Waste Incidents, Open File, 1978). The compound's persistence following migration is likewise shown by these incidents.

Although no comparable leachate data is currently available for naphthalene, the Agency believes that this constituent also may leach in harmful concentrations from the waste if not properly managed. Naphthalene is very water soluble, with solubilities ranging from 30,000 ug/l to 40,000 ug/l. In addition, naphthalene has been identified in finished drinking water, lakes, and rivers, demonstrating its ability to persist and to be mobile⁽⁴⁾. This information, naphthalene's solubility in water, and its presence in the tar in such high concentrations (22,000 ppm) make it likely that it will leach from the waste in potentially harmful concentrations if the waste is mismanaged, and will then be mobile and persistent, and so poses the potential for causing substantial hazard to human health and the environment.

Current practices of disposing of this waste in fact appear inadequate. Disposal of decanter tank tar-sludge in unsecured landfills or by dumping in the open makes it likely

that the hazardous constituents in the waste will leach out and migrate into the environment, possibly reaching and contaminating drinking water sources. Siting of waste management facilities in areas with highly permeable soils could facilitate leachate migration. As demonstrated above, the waste constituents appear capable of migration, mobility and persistence. Thus, if disposal sites are improperly managed or designed (e.g., lack adequate leachate collection systems), waste constituents could leach into soils and contaminate groundwater.

Health and Ecological Effects

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.⁽³⁾ 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⁽⁴⁾. Chronic poisoning may terminate fatally in some cases where

there has been extensive damage to the kidneys or liver.

OSHA has set a TLV for phenol at 5 ppm. Phenol is listed in Sax's Dangerous Properties of Industrial Materials as highly toxic via an oral route.(4) Sax also describes phenol as a co-carcinogen and a demonstrated carcinogen via a dermal route in studies done with laboratory animals. Additional information and specific references on the adverse effects of phenol can be found in Appendix A.

Naphthalene

Naphthalene is designated as 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/m³.

Sax lists naphthalene as moderately toxic via the oral route and warns that naphthalene is a demonstrated neoplastic substance via the subcutaneous route in experiments done on

laboratory animals⁽⁴⁾. Additional information and specific references on the adverse effects of naphthalene can be found in Appendix A.

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Primary Metals

LISTING BACKGROUND DOCUMENT

PRIMARY ALUMINUM REDUCTION

Spent potliners from primary aluminum reduction (T)

I. SUMMARY OF BASIS FOR LISTING

Primary aluminum metal is produced by the electrolytic reduction of alumina, an aluminum oxide. This process takes place in carbon-lined cast iron electrolytic cells known as "pots". After continued use, the carbon pot lining ("pot-liner") cracks, and must be removed and replaced with a new potliner.

The Administrator has determined that these used potliners ("spent potliners") are 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. Spent potliners from primary aluminum reduction contain significant amounts of iron cyanide complexes. EPA has detected iron cyanide complexes (expressed as cyanides) in spent potliners in significant concentrations.

Note: The Agency is aware that there are other solid wastes generated by the primary aluminum reduction process, and is currently investigating these wastes to determine whether to list them as hazardous in the future.

2. The aluminum reduction industry typically either stores spent potliners in unprotected piles outside (prior to reprocessing) or dumps them in the open. Part or all of the cyanide contained in the spent potliners can be expected to be released into the environment if spent potliners are dumped in the open, stored without protection in the open or otherwise improperly managed. Available data indicates that significant amounts of free cyanide and iron cyanide will leach from potliners if the spent potliners are stored or disposed of in unprotected piles out-of-doors and exposed to rainwater. In addition, in the presence of sunlight, the iron cyanides may decompose to release highly toxic hydrogen cyanide into the environment. Iron cyanide complexes are toxic and free cyanide is extremely toxic to both humans and aquatic life if ingested.
3. One major damage incident has been reported which is attributable to the improper disposal of spent potliners, demonstrating migration, mobility and persistence of waste constituents, and demonstrating as well that substantial hazard can result from improper management of this waste.
4. In 1977, the primary aluminum reduction industry generated an estimated 191,000 MT of spent potliners per year (approximately 6,366 MT per average-sized plant). This figure is expected to increase to 243,000 MT (approximately 8,100 MT per plant) by 1983. Generation of such large quantities of waste increases the potential for hazard if mismanagement should occur and is a further justification for listing these wastes as hazardous.

II. SOURCES OF THE WASTE AND TYPICAL DISPOSAL PRACTICES

A. Profile of the Aluminum Reduction Industry

Primary aluminum plants convert aluminum oxides into aluminum metal. Currently, there are 30* primary aluminum plants, located in 16 states, operating in the United States.

The primary aluminum industry currently produces approximately 5 million MT of primary aluminum per year (100,000 to 150,000 tons per year for an average-size plant). Pro-

*One other plant operates on a stand-by basis.

duction has been increasing for many years and is expected to reach 7 million MT per year by 1985.(7)

B. Manufacturing Process

Aluminum metal is produced almost entirely by the Hall-Heroult process. In this process, alumina, an aluminum oxide is reduced to aluminum metal in carbon-lined cast iron electrolytic cells known as "pots". The carbon potlining ("potliner") acts as the cathode of the cell; petroleum coke and pitch act as the anode; and cryolite, calcium fluoride, and aluminum fluoride are used as the electrolyte. When an electric current is passed through the pots, the alumina is reduced to aluminum metal. The molten aluminum is periodically drawn off as it accumulates in the bottom of the pots.

During the reduction process, iron cyanide complexes form in the potliners. The chemical/physical mechanism by which these compounds are produced is poorly understood(4); however, it is generally agreed that the iron cyanide compounds are produced in all cases(7).

C. Waste Generation and Management

After continued use, potliners crack, causing the molten aluminum in the pots to become contaminated with iron from the cast iron pots. At this point, the cracked potliners ("spent potliners") must be removed from the pots and replaced with new carbon potliners(1).

In 1974, the primary aluminum industry generated approximately 159,000 MT of spent potliners (approximately 5,300 MT for an average sized plant). By 1977, the industry

was generating an estimated 191,000 MT of spent potliners per year (6,366 MT per average facility)(1). This figure is expected to increase to 243,000 MT by 1983(1).

Spent potliners are either processed to recover cryolite (which saturates the potliners during the reduction process)*/ or disposed of immediately.(1,7) Those spent potliners which are reprocessed are usually stored on-site out-of-doors in uncovered piles(1,3,4,7), sometimes for periods of up to five years or more before reprocessing.(7) Spent potliners which are disposed of immediately are generally dumped in the open, either off-site or on-site.(1,3,4,7) No site preparation other than tree and shrub removal is commonly practiced(7). One company also has been reported to dispose of spent potliners in a lagoon, along with industrial sludge.(7)

D. Hazardous Properties of Spent Potliners

Spent potliners contain iron cyanide complexes. As noted above in Section B, these complexed cyanides are generated during the reduction process, and are believed to be present in all spent potliners. Analyses of leachate from piles of spent potliners (discussed below) confirm the presence of iron cyanide and free cyanide in the spent potliners(2,3,4,5). These concentrations are indicative of a potential for hazard, since these complexed cyanides are capable of migration as highly toxic free cyanides. Furthermore, iron cyanides themselves are toxic.

*/The Agency has information indicating that the wastewater from the cryolite recovery process contains high concentrations of cyanide. This waste stream is, therefore, being considered by the Agency as a candidate for future listing. Further information is solicited.

The following discussion demonstrates that cyanides are present in these wastes in substantial concentrations, and that, if the wastes are mismanaged, cyanide may migrate as both free and complexed cyanide, and may be mobile and persistent enough to reach environmental receptors via groundwater, surface water and air exposure pathways in concentrations sufficient to create a substantial hazard. Indeed, one damage incident involving spent potliners confirms that these wastes can cause substantial hazard if mismanaged.

A. Waste Composition and Migratory Potential of Waste Constituents

The Agency does not presently possess reliable data on iron cyanide concentrations in spent potliners themselves, but concludes that the concentrations of cyanide in potliners are substantial, based on cyanide concentrations in leachate from potliners. These data further demonstrate that the iron cyanide in the waste may migrate as highly toxic free cyanide in high concentrations in leachate or surface runoff. Monitoring samples taken by Kaiser Aluminum and Chemical Company in 1976 (10) confirm that free cyanide may migrate from this waste in high concentrations upon exposure to leaching media. These data indicate 2500 mg/l of free cyanide (13,000 mg/l total cyanide) in potlining slab liquor samples (the runoff from concrete slabs on which spent potliners are placed during open storage), and 1200 mg/l free cyanide (9000 mg/l total cyanide) in pot soaking pit liquor sample (liquor

left after spraying pots to facilitate removal of the liner)(10). That these concentrations pose very high potential for hazard is indicated by the fact that exposure to 300 ppm of cyanide will cause death to humans in minutes (see p. 9 below).

Furthermore, in a paper entitled "Development of a Method for Detoxification of Spent Cathode (potliner) Leachates", Comalco Aluminum personnel stated, " The storm water leachate from spent reduction cell cathodes (spent potliners) stored uncovered in the open typically contains unacceptably high levels of cyanides."(4). Table 1 of this paper shows spent potliner leachate to contain 200 mg/l */ of free cyanide and 2000 mg/l complexed cyanides prior to leachate treatment.

A third source likewise identifies substantial concentrations of complexed cyanides in leachate from spent potliners. The Kaiser Aluminum and Chemical Company collected and analyzed samples of pondwater from a pond that collects rainwater runoff from spent potliners which are discarded in a 10-acre dump next to its Chalmette, LA plant. Kaiser reported that pond liquor contains complexed cyanide in concentrations ranging from 50-700 ppm.(3,9) The chemical analyses of the pond liquor samples show concentrations of 100-350 ppm cyanide.(9)

Thus, both extremely toxic free cyanide and less toxic iron cyanides are capable of migrating from spent potliners in

*/The table, in fact, does not give units of measurement, but the actual values indicate that the units are mg/l.

substantial concentrations if the waste is exposed to leaching media. Migration of free cyanides may also occur via an airborne route. Iron cyanide has long been known to undergo photodecomposition leaving extremely toxic hydrogen cyanide and free cyanide decomposition byproducts.(8,13,14,15,16)*/
Hydrogen cyanide will then enter the atmosphere, where it is both mobile and persistent.(17) **/

Once free cyanide migrates from the waste it is likely to be quite mobile in soils. Cyanide has been shown to move through soils into groundwater.(12) Disposal of these wastes in the open, a present waste management method, could therefore lead to release of free cyanides and subsequent migration through soils to groundwater. (Migrating iron cyanide, on the other hand, has limited mobility in soils, but, as shown above, can photolyse to form mobile cyanide and hydrogen cyanide.)

Thus, these wastes may potentially release high concentrations of cyanide into water and (to a lesser extent) air, should mismanagement occur. Current waste management practices appear to allow a strong possibility of migration of cyanide i.e., spent potliners are often simply dumped in the open. Spent potliners being stored for cryolite recovery are also piled in the open without cover, sometimes for periods of up to five years (see p. 4 above). The Agency believes that substantial hazard could result from these

*/These sources do not indicate a degradation rate constant.

**/Hydrogen cyanide is reported to be resistant to naturally occurring wavelengths reaching the earth's surface.(17)

types of waste management practices, in light of this waste's potential to release free cyanide, and cyanide's mobility and persistence following release.

An actual damage incident involving spent potliners confirms this judgement. Kaiser Aluminum's Mead Works is situated 150 feet above the Spokane aquifer which is used for private wells and which drains into the Little Spokane River.(5) Leachate from a lagoon containing potliners and sludge leached through the ground and contaminated the aquifer with cyanide.(5) Eighteen wells were contaminated, some having cyanide levels in excess of 1,000 ppb.(5) Kaiser had to provide alternative sources of drinking water to the affected owners and to upgrade and seal the leaking lagoon.(5)

A further reason for listing spent potliners as hazardous is the quantity of waste generated. Approximately 191,000 MT of spent potliners were generated by the aluminum industry in 1977 and this figure is expected to increase substantially (see p. 3). Thus, large amounts of cyanide are available (in light of the high concentrations in leachate) for environmental release. These large quantities pose the danger of polluting large expanses of ground and surface waters, and an increased likelihood of reaching environmental receptors, in light of cyanide's mobility in water and air. Contamination also could occur for long periods of time, since large amounts of pollutants are available for environmental loading. Attenuative capacity of the environment

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 harmful constituents in the waste and, in the Agency's point of view, further justify a "T" listing.

Hazards Posed by Harmful Constituents

Cyanide is extremely toxic when it is ingested in free form and less toxic when ingested in complex form. (Appendix A). Free cyanide can cause death in humans and aquatic life. In its most toxic form, cyanide can be fatal to humans in a few minutes at a concentration of 300 ppm. While recovery from non-fatal poisonings is generally rapid and complete, fatal exposure levels are low. (App. A)

The Public Health Service recommends 0.2 mg/l as the acceptable level of cyanide for water supplies and EPA has recommended that this level be used as the ambient water quality standard under the Clean Water Act. The Canadian government has set a similar criterion. OSHA has regulated exposure levels for the workplace. Finally, final or proposed regulations of the states of California, Maine, Maryland, Massachusetts, Minnesota, Missouri, New Mexico and Oregon define cyanide-containing compounds as hazardous waste or components thereof. See Appendix A for references and additional information on cyanide.

Response to Comments

On August 22, 1979, EPA proposed to list spent potliners as a hazardous waste (44 FR 49404). No information was submitted during the public comment period that disagreed with the conclusion that spent potliners are hazardous as defined by the proposed regulation. The Anaconda Company stated however, that the particular disposal practices, coupled with the physical and geologic conditions at its two primary aluminum smelters produce "no significant release of any constituent from the spent potliners into an underground water supply." (6). Anaconda indicates that coal (not water) underlies its Kentucky disposal site, that there is little rain at its Montana site. It concludes that the standards for each disposal site should be established separately.

The conditions at any particular disposal site do not, however, change the initial determination of whether or not a waste is hazardous. A waste is listed as hazardous if it may pose a substantial threat to human health and the environment if it is mismanaged. Anaconda implicitly concedes that if the constituents released from spent potliners entered a drinking water reservoir, such a threat would exist. The individual circumstances of a particular disposal site will be addressed when a permit is issued, and are other-

wise taken into account in many of the standards contained in the recently promulgated Parts 264 and 265 (see, e.g., §265.90(c), which provides for a waiver of the groundwater monitoring requirement if a facility owner/operator demonstrates "that there is a low potential for migration of hazardous waste or hazardous waste constituents from the facility via the uppermost aquifer to water supply wells ... or to surface water").

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LISTING BACKGROUND DOCUMENT

PRIMARY SMELTING AND REFINING OF FERROALLOYS*

Emission control dust/sludge from ferromanganese (FeMn) production in electric furnaces (T)

Emission control dust/sludge from ferrochromium (FeCr) production in electric furnaces (T)

Emission control dust/sludge from ferrochromium-silicon (FeCrSi) production in electric furnaces (T)

I. Summary of Basis for Listing

The emission control dusts/sludges from the production of ferromanganese, ferrochromium and ferrochromium-silicon are generated when particulates entrained in the reaction gases given off by electric furnaces during the smelting process are removed by air pollution control equipment. Dry collection methods generate dust; wet collection methods result in 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 from ferromanganese and ferrochromium production contain significant concentrations of the toxic heavy metals chromium and lead, and emission control dusts/sludges from production of ferrochromium silicon contain significant concentrations of chromium.

*The Agency has recently obtained information indicating that wastes generated by the ferroalloys industry are likely to contain substantial concentrations of polycyclic organic several carcinogenic compounds (5). For this reason, EPA will expand the listing for the ferroalloys industry if further studies show that such wastes pose a hazard to human health and the environment.

- 2) Significant concentrations of chromium and lead have been shown to leach from various samples of ferromanganese and ferrochromium wastes subjected to extraction procedures, while significant concentrations of chromium have been shown to leach from samples of ferrochromium/silicon waste subjected to the same extraction procedures.
- 3) A large quantity (a combined total of approximately 120,000 tons) of these wastes is generated annually. There is thus a risk of large scale contamination of the environment if the wastes are mismanaged. Lead and chromium persist virtually indefinitely in the environment, posing the further threat of long-term contamination.
- 4) The wastes typically are disposed of by dumping in the open, in landfills or in unlined lagoons. Thus, the possibility exists for the migration in harmful concentrations of lead and chromium to groundwater or surface water.

II. Sources of the Waste and Typical Disposal Practices

A. Industry Profile and Manufacturing Process The

ferroalloys industry produces a variety of ferroalloys for use in the manufacture of iron, steel and non-ferrous metals (1). In May, 1980, eight companies produced ferrochromium, ferrochromium-silicon or ferromanganese in electric furnaces. Those producers are listed in Table 1 (5). It should be noted that companies may frequently change their product lines and put furnaces in or out of service according to product demand or operating requirements.

Ferrochromium, ferrochromium-silicon and ferromanganese are generally produced by carbothermal smelting in electric submerged-arc furnaces (some ferromanganese is also produced in blast furnaces). The raw materials used most often include

Table 1 - Producers of FeMn, FeCr or FeCrSi in
in the United States May, 1980 (5)

<u>Producer</u>	<u>Products</u>
CHROMASCO Woodstock, TN.	FeCr
INTERLAKE Beverly, OH.	FeCrSi, FeCr
MACALLOY Charleston, SC	FeCr
OHIO FERROALLOYS Philo, OH.	FeMn
SAMANCOR Rockwood, TN.	FeMn
SATRALLOY Steubenville, OH.	FeCr, FeCrSi
SKW ALLOYS Calvert City, KY. Niagara Falls, NY.	FeMn FeCrSi
UNION CARBIDE Marietta, OH. Portland, OR	FeMn, FeCr FeMn

mineral ores and concentrates of manganese, chromium and silicon, steel turnings and reducing agents such as coke, coal and wood chips (2). Feed materials are charged to the furnace on either a continuous or intermittent basis. The molten alloy collects at the bottom of the furnace and is removed to a cooling area.

B. Waste Generation

The process of reducing metallic ores to a metallic state generates large quantities of carbon monoxide along with other gases from moisture in the charge materials, reducing agent volatile matter, thermal decomposition products of the raw ore and intermediate products of the reaction (1). The gases carry fumes from the high temperature regions of the furnace and entrain fine particles of the charge materials. Particulate matter, which contains lead and chromium originally present in the charge materials, is removed from the gases by baghouse collection systems, electrostatic precipitators, or scrubbers. Wastes are collected from baghouses and precipitators as dusts and from scrubbers as sludges (2). These emission control dusts/sludges are the waste streams of concern. The Ferroalloys Association estimates that approximately 120,000 tons of these wastes are generated annually (2).

C. Current Disposal Practices

Dusts typically are dumped directly on land or disposed of in landfills (2,3). Dusts from the production of different

ferralloys are generally mixed and disposed of together.
 (Comments of the Ferroalloys Association, January 9, 1979.)
 Sludges usually are sent to unlined lagoons for settling;
 the sediments are dredged periodically and dumped on land
 (3). Waste piles in disposal areas can approach 250 feet in
 places, and the depth of disposal lagoons may approach 25
 feet (2).

III. Hazardous Properties of the Waste

Ferroalloy production emission control dusts and sludges consist primarily of sub-micron particles composed of oxides of various elements, including lead and chromium (3). The Agency has data from two sources which indicate that substantial amounts of lead and chromium are contained in ferromanganese and ferrochromium dusts/sludges, while dusts and sludges from ferrochromium-silicon production contain substantial concentrations of chromium. The data are presented in Tables 2 and 3.

Table 2. Concentrations of Lead and Chromium in Ferroalloys Dusts/Sludges (3).

Product	Sample Source	Cr(ppm)	Pb(ppm)
Ferromanganese	Baghouse (dust)	32	6000
	Scrubber (sludge)	18	5000
Ferrochromium	Electrostatic precipitator (dust)	3,390	300
Ferrochromium-silicon	Baghouse (dust)	41	--

Table 3. Concentrations of Lead and Chromium in Particulate Matter Generated During Production of Ferroalloys† (1).

Product	Sample Source	Cr(ppm)	Pb(ppm)
Ferromanganese	Scrubber stack outlet	<80	1,130
Ferrochromium	Furnace	140,000	--
	Electrostatic precipitator (dust)	40,000	1,000
Ferrochromium-silicon	Furnace	14,100	<10
	Baghouse inlet	4,400	--

†Most of the samples are of particulate matter collected from the furnace emissions prior to cleaning in an air pollution control device. These samples should be similar to the dust or sludge generated by these types of furnaces since emission control equipment removes 95-99% of these contaminants prior to air emission. (Comments of Ferroalloys Association, June 7, 1977, App. B.) The sample of particulate matter from the FeMn scrubber stack outlet should indicate which pollutant species are present in the sludge or dust, although relative quantities may be different from those in the solid waste.

Simulated leaching data also indicate that lead and chromium are capable of leaching from these wastes in concentrations sufficient to create a potential for substantial hazard. Table 6 below shows distilled water and acetic acid extraction data supplied by the Ferroalloys Association for selected emission control dusts. In most cases, contaminant levels in leachate are one to two orders of magnitude in excess of drinking water standards.

The Agency also has extraction data showing high concentrations of the constituents of concern in a distilled water extract of the waste:

Table 6 - Waste Extraction Data for Ferroalloys Waste (2)

<u>Waste from FeMn Production</u>		<u>Extract Concentrations</u>	
<u>EPA EP Using H₂O</u>	<u>Drinking Water Standard</u>	<u>Cr</u>	<u>Pb</u>
Emissions Control Dust (Sx #1)	.05	1.4	2.0
Emissions Control Dust (Sx #2)		1.0	7.6
<u>EPA EP per 9/12/78 Draft (Acetic Acid Extractant)</u>			
Emissions Control Dust		.40	14.0
<u>Waste from FeCr Production</u>			
<u>EPA EP Using H₂O</u>			
Emissions Control Dust (Sx #1)		.65	<.10
Scrubber Dust (Sx #2)		<.10	<.10
<u>EPA EP per 9-12-78 Draft (Acetic Acid Extractant)</u>			
Scrubber Dust (Sx #2)		<.10	<.10
<u>Waste from FeCrSi Production</u>			
<u>EPA EP Using H₂O Only</u>			
Emissions Control Dust		2.0	<.10
<u>EPA EP per 9-12-78 Draft (Acetic Acid Extractant)</u>			
Emissions Control/Dust		2.4	.30

Source: Comment of the Ferroalloys Association, January 9, 1979.

Table 7 (3)

Product	Sample	ppm in distilled water extract	
		Cr	Pb
FeMn	Baghouse dust	0.2	560
FeCr	ESP dust	710	0.7
FeCrSi	Baghouse dust	190	1.5

The Agency frankly entertains some doubts as to the probity of the data in Table 7. For example, the chromium value for the FeCrSi baghouse dust waste extract exceeds the value given for the raw waste sample in Table 2 above (which was obtained during the same study.) Such a discrepancy can only be attributable to an error in the calculation or in the recording of data, or to the use of faulty analytical techniques. Since high concentrations (14,000 and 4,400 ppm) of chromium in the particulate matter given off during the production of ferrochromium-silicon are reported in Table 3, the Agency believes it likely that the 41 ppm chromium value shown in Table 2 is grossly understated. In any case, the Agency views this data, while hardly determinative, as at least corroborative of other data submitted by industry showing waste constituents capable of migration in potentially harmful concentrations.

Furthermore, groundwater monitoring performed by an independent laboratory for the Ferroalloys Association

indicates that lead, one of the two waste constituents of concern, can migrate from ferroalloy waste disposal sites and reach groundwater in harmful concentrations. Thus, groundwater monitoring in the vicinity of an "unlined disposal lagoon" on the site of an unidentified ferroalloy company revealed lead concentrations in groundwater exceeding the National Interim Primary Drinking Water Standard of .05 mg/l, as shown in Table 4. In the second test, apparently only one well was measured; no contamination was detected.

Table 4 - Monitoring Data From Groundwater Wells Surrounding An Unlined Disposal Lagoon Showing Lead Concentrations In Groundwater (Reference: Comments of Ferroalloys Association, June 29, 1979.)

Monitoring Location		
Test #1	<u>Distance from Lagoons, (Ft.)</u>	<u>Pb Concentration(mg/l)</u>
Lagoon Analysis	---	.03
#1 Well	100	.085
#2 Well	500	.105
#3 Well	200	.190
#4 Well	100	.085
#4 Well	1600	.090
<u>Test #2</u>		
Lagoon Analysis	---	.160
#8 Well	375	----

Without groundwater background monitoring data, it cannot be said with assurance that the disposal lagoon is the source of lead contamination. However, the comments do not indicate any other source of contamination, and the fact that monitored lead levels in groundwater levels appreciably exceeded levels in the lagoon could indicate that concentrated solids from the lagoon are leaching into groundwater.* Certainly, this data fails to support the Ferroalloys Association's claim that of an absence of environmental problems from current disposal practice. (Comments of Ferroalloys Association, June 29, 1979, p.3).

Ferroalloys Association also supplied monitoring data obtained from wells in the vicinity of a ferroalloy waste landfill (2). These data are shown in Table 5.

Although the monitoring results might indicate that this landfill does not contribute substantially to groundwater contamination (measurements from wells located downgradient from the landfill are similar to background levels), the Agency is unable to determine whether this is a valid interpretation of the data without considerably more information on the hydrogeological characteristics of the site, the placement, construction and operation of the monitoring wells, the types and compositions of the wastes in the landfill and the protocols utilized to obtain and analyze the groundwater samples. Sampling over a longer period is probably

*Thus, the unexplained "lagoon analysis" could be of liquid in the lagoon rather than settled solids.

Table 5 - Monitoring Data from Groundwater Wells Surrounding
a "Typical Landfill" Showing Lead Concentrations in Groundwater

Location Test
Test #1

Upgradient
Groundwater Background

Pb in Groundwater (mg/l)

Well #3	<.03
Well #4	.08

Downgradient of Landfill

Well #1	.08
Well #2	.06
Well #5	.03

Test #2
(1 month after #1)

Upgradient

Well #3	.07
Well #4	.05

Downgradient

Well #1	.08
Well #2	.10
Well #5	<.03

Test #3
(2 months after #1)

Upgradient.

Pb in Groundwater (mg/l)

Well #3	.08
Well #4	.08

Downgradient

Well #1	.05
Well #2	.03
Well #5	.04

Note: Chromium was also monitored at these locations (although not at the wells surrounding the lagoon in Table 4), but chromium concentrations did not exceed the National Interim Primary Drinking Water Standard.

also necessary. Based on the information provided, the Agency can only observe that lead concentrations in groundwater in the vicinity of this landfill frequently exceed the National Interim Primary Drinking Water Standard of 0.05 mg/l. Therefore a potential hazard appears to exist unless proper management of these wastes is assured.*

It should be noted that some of the wastes included in this listing may not fail the toxicity characteristic (even though leachate data indicates that lead and chromium in these wastes have substantial migratory potential). This does not preclude listing of the wastes. The Agency believes that there are factors in addition to metal concentrations in leachate which justify this listing. As indicated above, these wastes are generated in very substantial quantities and may contain high concentrations of lead and chromium. Industry data indicate that groundwater contamination from ferroalloy waste disposal may already have occurred. In addition, large amounts of these metals are available for potential environmental release. The large quantities of these contaminants pose the danger of polluting large areas of ground or surface waters if waste mismanagement occurs. Contamination could also occur over long periods of time since large amounts of pollutants, which, as heavy metals, persist virtually indefinitely, are available for environmental release. Attenuative capacity

* The Ferroalloys Association indicated that the waste dusts are believed to exhibit sealant properties when wetted, thereby reducing leaching. This data (particularly that in Table 4), however, suggests that any sealant properties of the waste are insufficient to prevent waste constituent migration.

of the environment surrounding the disposal facility could also be reduced or exhausted due to the large quantities of pollutants available.

Furthermore, current management practices may not be adequate to prevent leachate migration and subsequent groundwater and/or surface water contamination. Industry submissions indicate that disposal lagoons and landfills are generally unlined, and that no special steps are taken to impede leachate formation (although the dusts are reported to exhibit a sealant effect when wetted, this appears insufficient to prevent leachate formation and migration). As a result, these waste management practices may have the potential to allow release of harmful concentrations of contained toxicants, particularly if disposal occurs in areas with highly permeable soils, or where waste is directly exposed to groundwater due to the height of the water table. If wastes are disposed of where acid rain is prevalent, solubilization of toxic heavy metals is even more likely to occur. Uncontrolled surface run-off from the waste piles and overflow from lagoons might disperse the wastes and/or their toxic constituents in the surrounding area. If control practices are nonexistent or inadequate, contaminant-bearing leachate, run-off or impoundment overflow may reach ground and surface waters, polluting valuable drinking water supplies.

IV. Hazards Associated With Constituents of Concern

Ingestion of drinking water from ground and surface waters contaminated by lead and chromium threatens human

health; aquatic species exposed to the heavy metals may also be adversely effected. Chromium is toxic to man and lower forms of aquatic life. Lead is poisonous in all forms, and is one of the most hazardous of the toxic metals because it bioaccumulates in many 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. (see Appendix A) It also bioaccumulates in many species.

Contact with chromium compounds can cause dermal ulceration in humans. Data also indicate that there may be a correlation between worker exposure to chromium and development of hepatic lesions. Additional information on the adverse health effects of these elements can be found in Appendix A.

The hazards associated with lead and chromium-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 have been established pursuant to the Safe Drinking Water Act. The Occupational Health and Safety Administration has a final standard for occupational exposure to lead and a draft technical standard for occupational exposure to chromium. In addition, a national ambient air quality standard for lead has been announced

under the Clean Air Act. Final or proposed regulations of the States of California, Maine, Massachusetts, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define lead and chromium compounds as hazardous wastes or components of hazardous wastes (4).

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Comments and Responses

- o One comment stated that ferrochromium-silicon emission control dusts/sludges should not be listed because a discrepancy between the chromium concentrations reported in the original sample and the extract of that sample exists; 190 ppm were found in leachate but only 41 ppm in the original waste sample.

The Agency agrees that an error was made. The error might be due to faulty analytical techniques or to a mistake in calculating or recording data. As stated in the background document, however, data from another source indicates that chromium concentrations in ferrochromium silicon emission control dusts/sludges might be much higher. For this reason, EPA believes that the value of 41 ppm is understated and will continue to list this waste as hazardous.

- o The Ferroalloys Association stated that the extracts of ferroalloys emission control dusts/sludges which they obtained by performing the proposed extraction procedure were only slightly above the limits defined as hazardous in the proposed regulations and therefore the wastes should not be classified as hazardous.

It is unusual that the data supplied by the Ferroalloys Association shows significantly less leaching using the proposed Extraction Procedure than other data from a distilled water extraction since the EP is the more rigorous of the two methods. Because such large quantities of these wastes are generated and samples of the wastes leached chromium in excess of 100 times the National Interim Primary Drinking Water Standard when subjected to a distilled water extraction, the Agency has decided that the wastes pose a potential threat to

human health and the environment and therefore should remain on the hazardous waste list.

- o One comment indicated that the wastes are not hazardous because they are properly managed.

The purpose of the regulations developed pursuant to §3001 of RCRA is to define hazardous waste. The hazard posed by a waste due to potential mismanagement is only one factor in the determination that a waste should be listed as hazardous. Other factors such as the nature of the hazard must be considered. The Agency believes that the waste listed above contain significant amounts of lead and chromium which may leach from the waste matrix and migrate to ground and surface waters; therefore the waste poses a threat to human health and the environment.

- o One comment included ground water monitoring data which show that the hazardous constituents of the waste do not migrate from the waste.

The data were acquired over a short period of time (2 months) and may not be representative of contaminant migration over a period of years. In addition, no information on the site conditions in the lagoon and landfill which were monitored was included in the comment so the Agency is unable to determine whether these are typical disposal sites.

The Ferroalloys Association stated that emissions control dust behaves as a sealant when it attains a sufficiently high moisture content and therefore provides a barrier to migration of hazardous constituents.

No data were submitted to support this contention so the

Agency is unable to respond in detail to the comment. EPA solicits additional information on the overall effectiveness of emissions control dust/sludges as sealants, the amount of moisture required to make the wastes behave as sealants and the moisture content of landfilled dusts.

LISTING BACKGROUND DOCUMENT

GRAY AND DUCTILE IRON FOUNDRIES

Emission Control Dust from Gray and Ductile Iron Foundry
Cupola Furnaces (T) (Proposed)*

I. SUMMARY OF BASIS FOR LISTING

Emission control dusts from gray and ductile iron foundry cupola furnaces are generated when the heavy metal contaminants found in the raw material scrap are entrained in the cupola furnace fumes as metal oxides and are subsequently collected

*The present proposed listing is limited to gray and ductile iron foundries collecting emission control dust from cupola furnaces. The Agency also has information indicating that gray iron foundries using electric arc furnaces generate an emission control dust with high concentrations of heavy metals, particularly lead. See U.S. EPA, Office of Air Quality Planning and Standards, Electric Arc Furnaces Foundries/Background Information for Proposed Standards, (Draft Environmental Impact Statement), EPA-450/3-80-020a (1980), pp. 726-27 (available from EPA Office of Solid Waste).) EPA thus may broaden the listing in the future to include electric arc furnaces. Further, in the sampling study described in the note below, EPA will sample some emission control dusts from electric arc furnaces to determine whether these wastes should be listed as hazardous.

NOTE: The Agency has made two prior proposals to list iron foundry process wastes. The first proposed listing, undertaken largely in response to comments received by the State of New York and Chem-Nuclear Systems, Inc., was of "lead/phenolic sandcasting waste from malleable iron foundries". This proposal was later altered (and the comment period extended) to cover "lead-bearing wastewater treatment sludges from gray iron foundries", 44 Fed. Reg. 674451, November 26, 1979). The present document expands the November, 1979 proposed listing to encompass a limited class of iron foundry emission control dusts.

These changes in the proposed listings have prompted industry complaints of having to respond to a moving target, making it difficult to comment responsively to the successive proposals.

The Administrator has determined that the emission control dust collected from gray iron and ductile iron foundry cupola furnaces 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 or RCRA.

This conclusion is based on the following considerations:

1. Waste extracts from gray and ductile iron emission control dusts have been shown to release high concentrations of the heavy metals lead and cadmium. In all cases the concentration exceeded 100 times the drinking water standards for lead and cadmium, and in some cases exceeded 1000 times the standard.
2. Large quantities of these wastes are generated annually, increasing the quantity of lead and cadmium available for environmental release.
3. These wastes may be disposed of in wetland or discharge type areas, increasing the hazardous constituents' migratory potential.

The Agency is sensitive to these concerns. Moreover, the Agency presently is undertaking a sampling and analysis study of the gray iron foundry industry's emission control wastes. Data from the sampling study will be used to make a final determination of the regulatory status of emission control sludges (which wastes have already been proposed for hazardous waste identification), as well as the dusts proposed for listing in this document. The assistance of the foundry industry in undertaking this study is acknowledged and appreciated by the Agency.

The Agency, therefore, is not promulgating either listing (i.e. either emission control dusts or wastewater treatment sludges) in interim final form. Rather, both listings are proposals, and no final regulatory action will be undertaken until completion of the sampling study.

These wastes are of concern due to the presence of lead and cadmium in a form capable of migration in high concentrations.

II. SOURCES OF THE WASTE AND TYPICAL DISPOSAL PRACTICES

A. Profile of Gray and Ductile Iron Foundry Industry

Approximately 1166 gray iron foundries and 81 ductile iron foundries comprise these two industries (1). Although the foundries are located throughout the United States, a large portion of the plants are found in the Great Lakes area. Geographic distribution of gray iron and ductile iron foundries is shown in Table 1.

Gray iron is characterized by the presence of most of the contained carbon as flakes of free graphite in the as-cast iron. Gray iron is classified into ten classes based on the minimum tensile strength of a cast bar. The tensile strength is affected by the amount of free graphite present as well as the size, shape and distribution of the graphite flakes. Flake size, shape and distribution are strongly influenced by metallurgical factors in the melting of the iron and its subsequent treatment while molten, and by solidification rates and cooling in the mold (1).

Ductile iron (also known as nodular iron, spherulitic iron, etc.) is similar to gray iron composition with respect to carbon, silicon and iron content, and in the type of melting equipment, handling temperatures, and general metallurgy. The important difference between ductile and gray iron is that the graphite in ductile iron separates as spheroids or nodules (instead of flakes as in gray iron) under the influence of a few hundredths of a percent of magnesium in the composition.

Table 1 (1)

Distribution of Total Gray and Ductile Iron Foundries

	<u>Gray Iron</u>	<u>Ductile Iron</u>
New England	77	3
Mid-Atlantic	188	9
Great Lakes	386	20
Plains	141	8
South Atlantic	101	7
East South Central	89	13
West South Central	80	9
Mountain	27	1
Pacific	<u>77</u>	<u>11</u>
	1166	81

The presence of minute quantities of sulfur, lead, titanium and aluminum can interfere with and prevent the noduling effect of magnesium. Although the molten iron for conversion to ductile iron must be purer than for gray iron manufacture, a small quantity of cerium added with the magnesium minimizes the effects of impurities that inhibit nodule formation and make it possible to produce ductile iron from the same raw materials used for high grade gray iron manufacture (1). Single foundries therefore are capable of producing both gray and ductile iron. Furthermore, since the same types of raw materials are used to produce each type of iron, waste composition also tends to be similar.

The general procedure for manufacturing ductile iron is similar to that of gray iron, but with more precise control of composition and pouring temperature. Prior to pouring of metal into the molds (and in some cases during pouring) the metal is inoculated with the correct percent of magnesium, usually in a carrier alloy, to promote the development of spheroids of graphite upon cooling (1).

B. Manufacturing Process (1)

1. Overall Process Description

While specific procedures vary from foundry to foundry, the overall operations for producing iron castings are essentially the same. These procedures include sand preparation, mold and core making, metal melting and pouring, casting shakeout and cleaning and finishing.

In all types of foundries, raw materials are assembled and stored in various material bins. From these bins, a furnace charge is selected by using various amounts of the desired materials. This material is charged into a melting furnace and made molten through a heating process.

Simultaneously, molds are prepared. This process begins by forming a pattern (usually of wood) to the approximate final shape of the product. This pattern is usually made in two pieces that will eventually match to form a single piece, although patterns may be 3 or more pieces. Each part of the pattern is used to form a cavity in a moist sand media, and the two portions of the mold (called "cope" and "drag") are matched together to form a complete cavity in the sand media. An entrance hole (called a "sprue") is cut to provide the proper paths of molten metal introduction into the cavity. The mold is then ready to receive the molten metal. In die casting operations the mold cavity is formed in metallic die blocks which are locked together to make a complete cavity.

The molten metal is then "tapped" from the furnace into the ladle. The ladle and molds are moved to a pouring area and the metal is poured into the molds. The molds are then moved to a cooling area where the molten metal solidifies into the shape of the pattern. When sufficiently cooled, the sand is removed by a process known as "shake out". By violent shaking, the sand surrounding the metal is loosened and falls to the floor or conveyor that returns it to the sand storage area.

The cast metal object (casting) is further processed by removing the excess metal, and cleaned by various methods that complete the removal of the sand from its surface. In the case of die casting, where no sand is used, the cast object is removed from the die casting machine after cooling sufficiently to retain its shape. The casting is either further cooled by a water bath or is allowed to cool by air on a runout or cooling table. Depending on the final use of the casting, further processing by heat treatment, quenching, machining, chemical treatment, electroplating, painting or coating may take place. After inspection, the casting is then ready for shipping.

2. Types of Furnaces used in Gray and Ductile Iron Production (1)

Three types of melting furnaces are used for the production of gray iron and ductile iron; cupola, electric arc, and electric induction furnaces. EPA estimates that 95% of the furnaces used for producing gray iron and ductile iron are cupola furnaces, and the present document covers emission control dusts only from this type of furnace. The differences among the types of melting furnaces are discussed below.

a) Cupola Furnaces

The cupola furnace is a vertical shaft furnace consisting of cylindrical steel shell lined with refractories and equipped with a wind box and tuyeres for the admission of air. A charging opening is provided at an upper level for

the introduction of melting stock and fuel. Near the bottom are holes and spouts from removal of molten metal and slag.

Air for combustion is forced into the cupola through tuyeres located above the slag well. The products of combustion, i.e., particles of coke, ash, metal, sulfur dioxide, carbon monoxide, carbon dioxide, etc. and smoke comprise the cupola emissions. Air pollution emission standards require that these emissions be controlled, and both dry and wet control systems are utilized for this purpose.

b) Electric Arc Furnaces

An electric arc furnace is essentially a refractory hearth in which material can be melted by heat from electric arcs. The molten metal has a large surface area in relation to its depth, permitting bulky charge material to be handled. Arc furnaces generally are not used for nonferrous metals as the high point of the arc tends to vaporize the lower melting temperature metals. Arc furnaces are operated in a batch fashion with tap-to-tap times of 1-1/2 to 2 hours. Power, in the range of 500-600 kwh/ton, is introduced through three carbon electrodes. These electrodes are consumed in the process of passing the electric current through the scrap and metal into the molten batch. They oxidize at a rate of 5 to 8 kg per metric ton of steel (10.5 to 17 lbs/ton).

The waste products from the process are smoke, slag, carbon monoxide and dioxide gases and oxides of iron emitted as submicron fumes. Dry collection air pollution control

equipment (usually baghouse) is generally used to control electric arc furnace emissions (1).

c) Induction Furnaces

Induction melting furnaces have been used for many years to produce nonferrous metals. Innovations in the power application area during the last 20 years have enabled them to compete with cupolas and arc furnaces in gray iron and steel production. This type of furnace has some very desirable features. There is little or no contamination of the metal bath, no electrodes are necessary, composition can be accurately controlled, good stirring is inherent and, while no combustion occurs, the temperature obtainable is theoretically unlimited.

There are two types of induction furnaces: (a) coreless, which is a simple crucible surrounded by a water-cooled copper coil carrying alternating current, and (b) core or channel, in which the molten metal is channeled through one leg of a transformer ore. The induction furnace provides good furnace atmosphere control, since no fuel is introduced into the crucible. As long as clean materials such as castings and clean metal scrap are used, no air pollution control equipment is necessary. If contaminated scrap is charged or magnesium is added to manufacture ductile iron, air pollution control devices are required to collect the fumes that are generated.

C. Waste Generation and Management (1)

The cupola furnaces in gray and ductile iron foundries require emission control systems. Both wet and dry systems are utilized. Venturi scrubbers are used exclusively for wet

crubbing of cupola furnace fumes and baghouses are used exclusively for dry collection of emissions. The waste collected by dry systems (baghouse dust) is the waste of concern in this document.

The use of a baghouse involves the collection of particulate matter by entrapment of the particles in the fabric of a filter cloth that is placed across a flowing gas stream. These dust particles are removed from the cloth by shaking or back-flushing the fabric with air. The resulting dry dust is usually collected in bins or open trucks (2). It is then often mixed with other foundry wastes prior to ultimate disposal in landfills.

It is estimated that for gray and ductile iron foundries, 10-22 lbs. of emission control dust is generated for every ton of metal produced (14). Approximately 95% or 1185 foundries use cupola melting furnaces. A known 392 foundries use wet collection systems and therefore EPA assumes that the remaining 793 (~65%) use dry dust collection systems. In 1979, 16,741,000 tons of metal were produced by the industry (3). If 65% of this amount is assumed to be produced by the 65% of the gray and ductile iron plants that generate a dry dust, then a range of 54,000 to 120,000 tons of dust will be generated by the industry per year. This estimate is probably low (2).

Foundry wastes are land disposed (1). Wastes from many foundries are monofilled, but others are disposed at municipal or private sanitary landfills which also accept other types of solid waste (2). Disposal procedures include random dumping

and grading, combination with other municipal and industrial wastes, and grading upon deposition followed by application of earth and topsoil cover (2). The physical setting of the disposal sites varies; locations are generally selected on the basis of availability of land at an appropriate cost within a reasonable haul distance from the foundry. It has been a fairly common practice to dispose of foundry wastes in wetland or discharge type areas where waste materials can become saturated with surface waters or shallow groundwaters (2).

D. Hazardous Properties of the Wastes

1. Waste Composition

The Agency believes that these emission control dusts ordinarily contain high concentrations of lead and cadmium, and that these toxic metals are capable of migration in quantities sufficient to create a substantial hazard if the wastes are managed improperly.*

The following data support this conclusion. Gray and ductile iron foundry cupola furnace emission control dusts from three foundries operated by the Mead Corporation were tested using the EPA extraction procedure, and in all cases the extract contained lead and cadmium significantly in excess of 100 times the National Interim Primary Drinking Water Standard. These data are presented in Table 2 below.

* The raw materials used as charge account for the lead and cadmium present in the emission control dust. Automotive scrap is thought to be one principal source of heavy metal contaminants (14). If engine block is used as scrap charge, the source of lead may be paint, tetraethyl lead deposits or engine bearings. If auto bodies are used as scrap, the source of lead may be attributable to paint or, more likely, to solder used to fill in joints (15).

TABLE 2

FOUNDRY EP TOXICITY TEST SUMMARY (14)

	<u>Level of EP Toxicity</u>	<u>Detect- tion Limit</u>	<u>Green Sand Cupola Dust</u>	<u>Shell Mold Cupola Dust</u>	<u>Cupola Dust</u>			
					<u>Dry Dust</u>	<u>Dry Dust</u>	<u>Wet Dust</u>	<u>Dry Dust</u>
Location			LB	LB	AC	RD	RD	LB
Date Sampled			5-8-79	5-8-79	8-22-79	10-30-78	10-30-78	10-78
<u>Parameters</u>								
Cadmium (mg/l)	1.0	0.01	6.9	4.8	2.5	19.6	6.6	12.9
Lead (mg/l)	5.0	0.05	16.5	12.8	11.5	96.0	68.0	2.3

LB = Lower Basin Foundry (Gray and Ductile Iron)
AC = Archer Creek Foundry (Gray and Ductile Iron)
RD = Radford Foundry (Ductile Iron)

Note: Analysis for other heavy metals and the 129 priority pollutants revealed no significant concentrations of any of these parameters.

The charge for these foundries is believed to consist primarily of fairly high grade (clean) metal scrap from a number of sources (14). Facilities accepting lower grade scrap (such as automotive body scrap) could have higher concentrations of these metals in their emission control dusts.

These leachate extract results indicate strongly that improper management of the wastes could lead to migration of dangerous concentrations of cadmium and lead from the waste. A further concern in assessing potential hazards posed by these wastes is the possibility that existing disposal practices may not always be adequate, since disposal in wetlands and municipal landfills is said (in an industry publication) to occur. Since lead and cadmium appear to be present in these wastes in leachable form, waste disposal under conditions where leaching media are readily available could well lead to migration of contaminant-bearing leachate which can then migrate to ground or surface water. Disposal in acidic environments, such as landfills containing municipal refuse (another waste management practice known to occur (2)), could also lead to environmental release of dangerous concentrations of lead and cadmium. Improper disposal of these dusts can therefore result in contamination of ground and surface waters with 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.

In addition an inhalation hazard may be posed by management of this waste due to its fine particulate nature and due to the inhalation toxicity of the particulates. The dust could easily become airborne and cause damage to humans if the waste is not properly buried at the time of disposal. The waste also could pose an inhalation hazard during transportation if it is transported in open trucks and no precautions are taken to prevent dust from blowing freely.

These wastes also are believed to be generated in substantial quantities (see page 10 above). This is further cause for concern, since large amounts of the toxic constituents cadmium and lead 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 attenuative capacity of the environment surrounding disposal facilities 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 waste and further justify a hazardous designation.

2. Hazardous Properties of Waste Constituents

The cadmium and lead that may migrate from the waste to the environment as a result of improper disposal practices are heavy metals that persist in the environment and may contaminate drinking water sources for extremely long periods of time. Cadmium is toxic to practically all systems and

functions of the human organism (6). Acute poisoning may result from the inhalation of cadmium dusts and fumes (usually cadmium oxide) and from ingestion of cadmium salts (7). 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. Inhalation hazards are also possible through exposure to the airborne dust which contains lead oxide and cadmium oxide. 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 1970. Under §6 of the Occupational Safety and Health Act of 1970, a final standard for occupational exposure to lead has been established (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, Massachusetts, Minnesota, Missouri, New Mexico, Oklahoma and Oregon define cadmium and lead-containing compounds as hazardous wastes or components thereof (9).

EPA has proposed regulations that will limit the amount of cadmium in municipal sludge which can be landspread on crop land (10). 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) (11). EPA has prohibited ocean dumping of cadmium and cadmium compounds except as trace contaminants (12). EPA has also promulgated pretreatment standards for electroplaters which specifically limit discharges of cadmium to Public Owned Treatment Works (13).

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10. 44 FR 53449.
11. 44 FR 5434.
12. 38 FR 28610.
13. 40 CFR, Part 413.
14. U.S. EPA, RCRA Section 3001 Docket. Memorandum of meeting with Mead Corporation, June 25, 1980.
15. U.S. EPA, RCRA Section 3001 Docket. Memorandum of phone call from Russell Frye of Mead Corporation to Claire Welty. July 8, 1980.

V. Response to Comments

A number of comments have been received which address the Agency's proposed listing of wastewater treatment sludges from gray iron foundries. As noted above, the Agency is undertaking (with industry assistance), a sampling study of selected foundry wastes and does not plan to proceed to finalize this listing or to abandon the listing until the study is completed. The Agency does feel that it is necessary to restate its justification for proposing to list these wastewater treatment sludges, both to respond to criticism that the proposal lacks justification and to indicate our concern that these wastes could pose a very real hazard if disposed of improperly.

First, these waste sludges could contain large quantities of lead, a toxic element. EPA analyzed raw and treated wastewater samples from five plants. These data and resultant lead levels found in the sludge at these five plants are summarized as follows (1):

Plant	Lead Concentration in Raw Wastewater (mg/l)	Lead Concentration in treated Wastewater (mg/l)	Lead Concentration removed from wastewater(mg/l)	Flow (gal/ day)	Total Lead (pounds year)
A	40	2.2	37.8	4.8×10^4	3,800
B	54	0.9	53.07	3.86×10^5	42,700
C	29	1.4	27.6	4.24×10^5	24,400
D	100	8.5	91.5	1.13×10^6	216,000
E	140	0.87	139.13	7.49×10^4	21,700

Note: This type of mass balance approach provides an accurate indication of amounts of lead in the wastewater treatment sludge, since lead neither degrades nor volatilizes.

Thus, total potential environmental loadings of lead from these wastes appear to be high. Further, over 5 million wet tons of these wastes are generated annually on a national basis (1), increasing concern about total potential lead loadings.

Second, lead will be present in these wastes in higher concentrations than concentration of lead removed from the waste water, since the sludge will be dewatered, and the lead therefore concentrated, before disposal.

Third, an industry publication indicates that "(i)t has been a fairly common practice in disposal of foundry solid wastes ... to use wetland or discharge type areas. In areas such as these, waste material is often water-saturated from the presence of surface water or shallow groundwater". ("Foundry Landfill Leachages from Solid Wastes", American Foundrymen's Society, 1978.) Under these conditions, dangerous concentrations of lead could leach into ground and surface waters and reach environmental receptors.

o Industry has indicated that although lead is present in these sludges, it is present in a substantially immobile form. One of the purposes of the sampling study is assess the potential mobility of waste constituents. Although this is not the sole determinant of a waste's toxicity (see 261.11), it is certainly a significant factor in making a listing determination. Thus, the results of waste extract data from the upcoming sampling study will be taken into consideration in making a final listing determination.