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Agency

Office of Solid Waste
and Emergency Response
Washington, DC 20460

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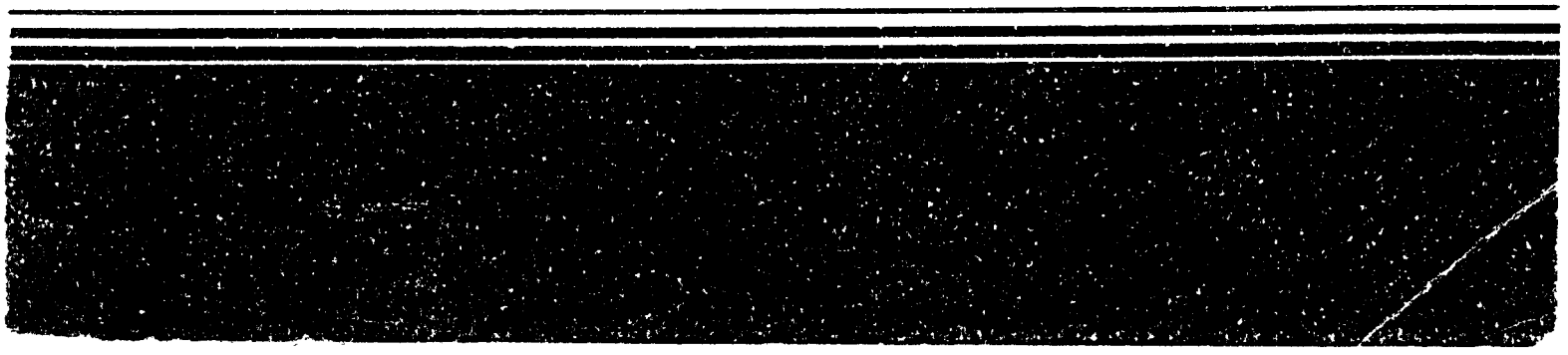
Solid Waste

EPA

Waste Minimization

Issues and Options

Volume II



Waste Minimization Issues and Options
Volume 2: Appendices A and B

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LIST OF APPENDICES

A. DATA BASES USED IN THIS STUDY

A.1 Description of Data Bases
A.2 Questionnaire for RIA Generator Mail Survey
A.3 Questionnaire for RIA TSD General Mail Survey
A.4 Questionnaire for Industrial Studies Data Base Survey

B. PROCESS STUDIES

B.1 Acrylonitrile Manufacture
B.2 Agricultural Chemicals Formulation
B.3 Electroplating
B.4 Epichlorohydrin Manufacture
B.5 Inorganic Pigments Manufacture
B.6 Metal Surface Treatment
B.7 Organic Dyes and Pigments Manufacture
B.8 Paint Manufacturing
B.9 Petroleum Refining
B.10 Phenolic Resins Manufacture
B.11 Printed Circuit Boards Manufacture
B.12 Printing Operations
B.13 Synthetic Fibers Manufacture
B.14 Synthetic Rubber Manufacture
B.15 1,1,1-Trichloroethane Manufacture
B.16 Trichloroethylene/Perchloroethylene Manufacture
B.17 Vinyl Chloride Monomer Manufacture
B.18 Wood Preserving
B.19 Good Operating Practices
B.20 Metal Parts Cleaning
B.21 Paint Application
B.22 Process Equipment Cleaning

APPENDIX A

DATA BASES USED IN THIS STUDY

A.1 Description of Data Bases

This study was based on information compiled from a variety of sources, including the Regulatory Impact Analysis (RIA) Mail Survey, Biennial Report Data Base, Industrial Studies Data Base, National Small Quantity Generator Hazardous Waste Survey, State information, industrial information, and other literature. This appendix contains descriptions of the computer data bases, how they are used, deficiencies or data gaps associated with them, and the extent to which these deficiencies can be rectified. We have also included copies of the survey forms used to collect data for the RIA Mail Survey and the Industrial Studies Data Base.

I. Regulatory Impact Analysis (RIA) Mail Survey

The RIA Mail Survey is a computerized data base that contains the results of a 1982 national survey of hazardous waste generators and treatment, storage, and disposal facilities (TSDFs). The survey, sponsored by the Office of Solid Waste, produced a statistically weighted data base containing more than 6,000 elements describing hazardous waste generation and management activities in 1981, including data on the volumes of waste that were generated, recycled, reused, and reclaimed. The survey identifies specific facilities and Standard Industrial Classification (SIC) codes that generate and recycle hazardous waste, and distinguishes between onsite and offsite treatment of recycled wastes.

In this study, the RIA Mail Survey is the basis for identifying trends in the generation and recycling of hazardous waste. The survey is the most comprehensive source of information on volumes of wastes being handled and recycled. Sample data have been extrapolated to the entire nation. All quantities were given in gallons per year and were sorted by the five waste categories (halogenated organics, solvents, metals, corrosives, and cyanides and other reactives); the SIC categories; and EPA's RCRA Codes (e.g., K011, D001). Because of the magnitude of the data base, the listing of industrial categories was screened to eliminate those source categories that generate or recycle relatively small quantities of waste material

(i.e., less than 50,000 gal/yr). For this study, we used data obtained from two sample populations surveyed by the RIA Mail Survey: (1) Generators and (2) Treatment, Storage, and Disposal (TSD) facilities. Both the generator and TSD survey forms are included in Appendices A-2 and A-3.

During our review of the data base, we identified certain ambiguities, gaps, and inconsistencies. Such limitations must be considered when these data are interpreted. Specifically, the restrictions include:

- Statistical Reliability of the Data Base. The statistical limitations of the data base have been well documented in the "National Survey of Hazardous Waste Generators and Treatment, Storage, and Disposal Facilities Regulated Under RCRA in 1981," which was prepared for EPA by Westat, Inc. in April 1984. This report states that ".....quantity estimates (or ratios of quantity estimates) are subject to considerably more estimation error than are estimates about the number or percentage of sites with certain characteristics." Skewed distributions of volumes of wastes handled by TSDFs and generators were, in fact, quite common. Also, because of the numbers of facilities surveyed, comparisons of the numbers of facilities that conduct certain practices, e.g., onsite vs. offsite recycling, may be limited to one or two data points. This can result in an inaccurate projection of the frequency of occurrence of a practice nationally.

- Age of the Data. The RIA Mail Survey, containing 1981 information, may be somewhat dated. Quantities of waste generated and treated may have, in certain instances, changed markedly over the past four years. Implementation of RCRA requirements and public concern about the impacts from land disposal have encouraged new technology and increased materials-handling capacity.

- Generation Rates. The generation survey requested respondents to provide a breakdown by percent of total waste that comprises "F" or "K," "P," "U," ignitable, corrosive, reactive, and EP-toxic wastes. Translating these divisions into the five waste streams of this waste minimization study (halogenated organics, solvents, metals, corrosives, and cyanides and reactives) presented difficulties in obtaining generation volumes for other than the characteristic wastes. The "F" or "K," "P," and "U" wastes could very easily fit into any or a few of the five waste categories. In addition to lack of generation volumes of solvents and halogenated organics, participants may have occasionally responded incorrectly; for example, in one particular instance for a specific SIC category, a total was given for the

volume of F or K waste generated. The same total was given for ignitable, and the same for corrosive. The respondent may have reasoned that his waste fit all three categories and entered the same percentage in each category. The result is that the value in the total waste column is the sum of all categories, thus misrepresenting the amount of waste the facility generated by three times. For those SIC categories in which only a few companies were surveyed (usually one or two), such responses can cause gross misinterpretations of volumes of waste generated for that particular industrial subcategory. In categories in which there are many respondents, such discrepancies are not as evident and are essentially "hidden in the noise."

- Regional Extrapolations. This study provides regional breakdowns of waste generation as well as national breakdowns. Unfortunately, regional breakdowns are not accurate because of the lack of data in some instances upon which to statistically base projections. For example, in Region II, three of the major TSD facilities in the State of New York were not surveyed. Reasonable extrapolations could be made on a nationwide basis, however. This deficiency may be rectified by relying on information from individual States as reported in the Biennial Report Data Base described below.

- Discrepancies in Recycled Proportions. Westat (1984) indicates that estimates of the proportion of generated wastes that are recycled may be inaccurate. "The proportion estimate is based upon the Generator Questionnaire, which understates the quantities of hazardous waste generated with onsite TSD facilities. To the extent that these generators recycle greater proportions of their hazardous wastes than does the generator population as a whole, the proportion is understated. To the extent that these generators recycle smaller proportions of their hazardous waste, the proportion is overstated."

- Inability to Determine True Waste Volumes. It is apparent that, on occasion, the reported volume generated and handled by a facility may be exaggerated. This sometimes occurred when the waste stream was diluted with water (this also contributed to the previously noted skewed data). A significant portion of the waste stream may not be recyclable because the stream is too dilute (with water). In order to properly evaluate the recyclability of a stream, additional information is needed on the makeup of the waste. Unfortunately, it is not possible to compare the quantities of wastes that are technically and practically recyclable, and those volumes that actually were recycled.

- Total Amount of Waste Landfilled, Treated, or Otherwise Handled Was Not Reported. The RIA General and TSD Mail Surveys present the total amount of waste (by SIC code) generated, shipped offsite, and recycled onsite or offsite. These surveys did not ask for the total amount of waste that is landfilled (onsite or offsite), treated, or otherwise handled. Examining the

other RIA Mail Surveys (e.g., Land Disposal, Treatment, and Incineration) will provide volumes of wastes handled in these ways, but such surveys do not provide information on a SIC level. Thus, the Land Disposal Survey can provide information on the amount of waste landfilled, but not the portions that came from SIC 28, 26, 35, etc. Total wastes and their handling methods and volumes can be obtained in this manner, but the Land Disposal Survey and other management practice-specific surveys do not survey the same population as the Generator Survey, so the results are not directly comparable.

- Inconsistencies in the Data Base. On rare occasions, data did not correlate. For example, in isolated instances, the sum of the wastes recycled onsite and offsite for an industrial category did not match the total waste recycled within that SIC. The problem is likely to be inherent in the data base. For example, a facility may have responded to the questionnaire by listing a quantity of waste that was recycled, but did not enter an estimate of the volume(s) recycled onsite or offsite.

- Facility Size Correlation. Information on size did not show a good correlation with the amount of waste generated. For each facility identified in the RIA Mail Survey, the number of employees at each facility was obtained from data compiled by Dun & Bradstreet. The resulting correlation between waste generated and number of employees per facility was 0.19, which is low. This has been partially rectified by providing information on the number of facilities nationwide within each SIC category for which waste generation volumes are presented.

II. Industrial Studies Data Base (ISDB)

The information contained in this data base was retrieved from questionnaires sent to industries under Section 3007 of RCRA. The ISDB contains data for 12 major industries within the Chemicals and Allied Products (SIC 28) industry, comprising approximately 300 facilities, 4,000 waste streams, 500 processes, and 1,000 products. It differs from the RIA Mail Survey in that it is structured to obtain information on the various processes within each of the industrial categories surveyed. (A survey form for the rubber and plastics industry is included as an example of the questions used to structure the data base. It is provided in Appendix A-4.) In addition, the waste stream data are more comprehensive, since they provide the constituent components of the waste streams and the percentage of each component to the total waste stream volume. More detailed information is

available in this data base on the type of recycling technologies used for the various waste streams and the final disposition of and uses for the recovered materials.

This data base also has its limitations, however, which include:

- Data Base Limited to Chemical and Allied Products (SIC 28) Industry. Only information from the chemical and allied products industry is included in this data base. Therefore, it is not representative of all industries.

- Lack of Information and Limited Access to Two Industrial Categories. Because of lack of information within 1 of the 12 industrial categories and limited access to another, we have determined that 10 of the 12 surveyed have data of potential use for this study.

- Limited Information on Metal and Cyanide/Reactive Wastes. Since the ISDB only contains information for the chemicals and allied products industries (SIC 2800s), information on the recycling of metals and cyanide/reactive wastes is limited, because these industries do not generate those wastes to any great extent.

Though metal and cyanide wastes may be underrepresented, the chemical manufacturing industries generate the largest fraction of hazardous waste according to other data sources.

III. National Small Quantity Hazardous Waste Generator Survey

This source contains the results of a national survey, sponsored by EPA's Office of Solid Waste, of small quantity generators (SQGs) undertaken by ABT Associates, Inc. between January 1983 and October 1984. The survey, distributed to nearly 50,000 selected generators, resulted in a data base comprising approximately 19,000 responses. The survey was designed to obtain a profile of generators and information regarding their hazardous waste streams and waste management practices. One hundred twenty-five standard industrial classification codes were selected and combined into 22 groups as industries of primary concern; data for these groups were statistically weighted in order to generalize from the sample population. For each industry group, the survey presents a breakdown of quantity of

waste generated by waste stream. It profiles the onsite and offsite management practices, including various recycling methods, according to the number of establishments and quantity of waste. In addition, three sizes of generators are distinguished: those producing less than 25 kilograms per month, those producing from 25 to 100 kilograms per month, and those producing from 100 to 1,000 kilograms per month. Waste stream-specific information on management methods, however, is only available for the six largest SQG waste streams. For these waste streams, the 22 industry groups are no longer distinct. Aside from the inherent discrepancies taken into account by its investigators, the survey has two apparent disadvantages for the purposes of this report, which is based on five major waste streams: lack of the waste stream-specific information and the fact that RCRA waste codes are not given.

IV. Biennial Report Data Base

The Biennial Data Base is an electronic data base containing 1983 Biennial Report Data Summaries from 45 States for hazardous waste treatment, storage, and disposal facilities. This electronic data base is managed by DPRA using the Office of Solid Waste Prime 2250 computer system.

The Biennial Report is designed to collect information on hazardous waste activities for generators and TSDFs. Individual generators and TSDFs are required to complete the appropriate form(s) providing general facility information, detailed information on quantities generated and handled by specific waste code, and the final disposition of the waste. The individual Biennial Report forms are collected by the State or Region every even numbered year and include information for the previous odd numbered year. A summary of the data is prepared and the Biennial Report Summary is submitted to EPA.

The types of data contained in the Biennial Report Summaries and input to this data base include: lists of hazardous waste generators and treatment, storage, and

disposal facilities onsite, offsite, and both onsite and offsite (with "offsite" defined as a TSDF where no waste was generated at the facility itself); quantities of waste generated by EPA waste code; quantities of waste shipped out-of-State and brought into the State; quantities of waste (identified by RCRA waste codes) managed by specific methods (e.g., treatment, landfill, incineration).

The main deficiencies in the Biennial Data Base involve the design of the Biennial Report forms used to collect the raw data and the manner in which data are submitted by States to EPA. These limitations include:

- Limited Information on Recycling. The EPA Biennial Report forms for 1983 did not differentiate between recycling and other forms of treatment. Only six States requested a breakdown between recycling and treatment on their forms. The remainder lump recycling into one of at least four treatment codes: tank, surface impoundment, incinerator, or "other."

- Generation Quantities. The generation values in this data base may have been overreported. The smallest reporting unit is one ton unless the generation rate is indeed zero; thus, 100 pounds is reported as one ton.

- Handled Quantities Are Based on Final Disposition. The reported waste handling method for a particular waste represented the final disposition for that waste during 1983. If a waste was treated prior to disposal (i.e., final disposition), this information would not have been reported. As a result, treatment values may be underreported.

- Waste Volumes Generated on a State Level. Waste volumes generated are presented in this data base on the State level, not on a facility level. The numbers presented are for the waste types or total wastes generated within that State, but the numbers cannot be matched to a facility ID. Information at the facility ID level is limited to questions that can be answered yes or no (e.g., Did you ship wastes offsite? Did you land dispose waste?) Thus, it is not possible to match waste generation volumes with facility IDs and then subsequently match these IDs with SIC codes in the RIA Mail Survey.

- Double-Counting When Waste Volumes Are Broken Down by Management Practice. Waste volumes handled by various waste management practices are not broken down as to the portion that is kept in-State, and the amount shipped out of State. Thus, for a given State, a quantity of waste that is reported to be landfilled offsite may contain portions that have been shipped from other States, and which have been reported in that State as also having been shipped offsite. As a result, there is a built-in mechanism for double-counting.

- California's Different Treatment Codes. The California Department of Health Services has established its own biennial report with more detailed waste treatment codes and information on recycling. However, California waste codes, which focus on constituents rather than waste streams, are independent of EPA codes, and there is no simple translation between the two. Both California's and the States' data bases fail to break down the hazardous waste facilities into SIC codes.

States have been contacted and several have provided status reports with information on their hazardous waste management and alternative treatment methods. Overall, the Biennial Report Data Base is a thorough inventory of EPA-coded wastes generated and handled by hazardous waste facilities.

OMB # 2050-0024
Expires: December 31, 1982

U.S. ENVIRONMENTAL PROTECTION AGENCY
HAZARDOUS WASTE GENERATOR QUESTIONNAIRE

PLEASE RECORD THE FOLLOWING INFORMATION ONLY IF DIFFERENT FROM LABEL ABOVE.

Name of Installation: _____

Installation's EPA Identification Number: |__|__|__|__|__|__|__|__|__|__|__|__|

Mailing Address: _____
STREET OR P.O. BOX

_____
CITY STATE ZIP CODE

1. Please record the location of this installation.*

**PLEASE GIVE THE ACTUAL PHYSICAL LOCATION, RATHER THAN THE MAILING ADDRESS, OF THE INSTALLATION CORRESPONDING TO THE EPA IDENTIFICATION NUMBER ABOVE.

ADDRESS: _____

CITY: _____ COUNTY: Q1A

STATE: _____ ZIP CODE: Q1B

2. Whom should we contact for follow-up at this installation?

NAME: _____ Q2 (not covered)

TITLE: _____

PHONE NUMBER: |__|__|__| - |__|__|__| - |__|__|__|__| EXTENSION: |__|__|__|__|
AREA CODE

3. In the table below, please list the primary SIC (Standard Industrial Classification) code of this installation, and up to three secondary SIC codes, if more than one code is required to describe this installation. [IF YOU DO NOT KNOW THE SIC CODE FOR THIS INSTALLATION, PLEASE SELECT THE MOST APPROPRIATE CODE(S) FROM THE SIC CODE LIST INCLUDED IN APPENDIX C OF THE GENERAL INSTRUCTIONS]

a. Primary SIC code	Q3A	71-77
Secondary SIC codes [PLEASE LIST IN DESCENDING ORDER OF IMPORTANCE]:		
b.	Q3B	78-81
c.	Q3C	82-85
d.	Q3D	86-89

4. Please indicate the type(s) of hazardous waste activity(ies) in which this installation was engaged during the 1981 calendar year. [CIRCLE ALL CODES THAT APPLY]

a. Hazardous waste generation.	Q4A	01	90-91
b. Hazardous waste treatment	Q4B	02	92-93
c. Hazardous waste storage	Q4C	03	94-95
d. Hazardous waste disposal.	Q4D	04	96-97
e. Hazardous waste transportation. . . .	Q4E	05	98-99
f. Recycling of hazardous waste.	Q4F	06	100-101
g. None of the above	Q4G	07	102-103

IF CODE "01" IS CIRCLED, PLEASE SKIP TO QUESTION 7.

5. Which of the following statements best describes the hazardous waste generation activities at this installation? [CIRCLE ONLY ONE CODE] Q5

a. No hazardous waste was generated during 1981, none was generated during the five years prior to 1981, and hazardous waste is not expected to be generated in any quantities during the five years following 1981. 01

b. No hazardous waste was generated during 1981, none was generated during the five years prior to 1981, but hazardous waste is expected to be generated at some point during the five years following 1981. 02

c. No hazardous waste was generated during 1981, but hazardous waste was generated at some point during the five years prior to 1981, and hazardous waste is expected to be generated at some point during the five years following 1981 03

d. No hazardous waste was generated during 1981, but hazardous waste was generated at some point during the five years prior to 1981. Hazardous waste is not, however, expected to be generated again at this installation during the five years following 1981 04

e. Hazardous waste was generated in 1981, but no more than 1000 kg, of hazardous waste (and no more than 1 kg. of acutely hazardous waste) was generated during any single month (small quantity generator). 05

f. Hazardous waste was generated in 1981, but all quantities of the hazardous waste generated were or will be used beneficially, reused, recycled, or reclaimed within one year of generation. 06

g. Hazardous waste was generated in 1981, but all quantities were generated in farming operations and disposed of in accordance with applicable RCRA regulations 07

h. Hazardous waste was generated in 1981, but the waste has since been exempted from regulation or de-listed as a hazardous waste under RCRA 08

i. Hazardous waste was generated in 1981, and at least 1000 kg. of hazardous waste (or 1 kg. of acutely hazardous waste) was generated during a single month [SKIP TO QUESTION 7]. 09

104-105

6. Why was a Notification Form submitted to EPA indicating that hazardous waste would be generated at this installation?

Q6A

Q6B

106- 7

108- 9

PLEASE SIGN THE CERTIFICATION STATEMENT ON PAGE 22 OF THIS QUESTIONNAIRE AND RETURN THIS FORM TO EPA.

7. What was the total quantity of hazardous waste generated at this installation during the 1981 calendar year? [ENTER QUANTITY AND CIRCLE UNIT CODE]

NOTE: STATE THE QUANTITY OF WASTE GENERATED IN PRODUCTION OR OTHER PROCESSES PRIOR TO THE ALTERATION OF SUCH WASTES THROUGH TREATMENT (SUCH AS DEWATERING) OR OTHER WASTE MANAGEMENT PROCESSES. INCLUDE WASTES THAT WERE OR WILL BE USED, RECYCLED, OR RECLAIMED, OR SUBSEQUENTLY RENDERED NONHAZARDOUS.

TOTAL QUANTITY OF HAZARDOUS WASTE GENERATED IN 1981: Q 7 /110-118

[CIRCLE ONE]:

Metric tonnes. Q.7.4.C. 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: _____ 04 /119-120

8. What quantity of the hazardous waste that was generated at this installation during 1981 (as specified in Question 7) was or will be used, reused, recycled, or reclaimed (either on site or off site)? [ENTER QUANTITY AND CIRCLE UNIT CODE]. /021

QUANTITY GENERATED IN 1981 THAT WAS/WILL BE USED, REUSED, RECYCLED, OR RECLAIMED: Q 8 /15-24

[CIRCLE ONE]:

Wet metric tonnes. . . . . Q 8 4 C 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: _____ 04 /25-26

9. Of the total quantity of hazardous waste generated at this installation (as specified in Question 7), please indicate the percentage handled as hazardous for the following reasons:

NOTE: TOTAL MAY EXCEED 100% BECAUSE SOME WASTE MAY BE CLASSIFIED AS HAZARDOUS FOR MORE THAN ONE REASON. HOWEVER, THE TOTAL SHOULD NOT BE LESS THAN 100% OF THE QUANTITY OF HAZARDOUS WASTE GENERATED THAT IS SPECIFIED IN QUESTION 7.

REASON FOR HANDLING AS HAZARDOUS	PERCENT OF HAZARDOUS WASTE GENERATED	
a. Because it was listed with an EPA Waste Number beginning with F or K	Q9A %	27-29
b. Because it was listed with an EPA Waste Number beginning with P.	Q9B %	30-32
c. Because it was listed with an EPA Waste Number beginning with U.	Q9C %	33-35
d. Because it exhibited the characteristic of Ignitability (EPA Waste Number D001)	Q9D %	36-38
e. Because it exhibited the characteristic of Corrosivity (EPA Waste Number D002).	Q9E %	39-41
f. Because it exhibited the characteristic of Reactivity (EPA Waste Number D003)	Q9F %	42-44
g. Because it exhibited the characteristic of EP Toxicity (EPA Waste Numbers D004-D017). . . .	Q9G %	45-47
h. Because it was identified or listed as a hazardous waste by a state	Q9H1 %	48-50
[DESCRIBE WASTES INCLUDED IN THIS CATEGORY]: _____ _____	Q9H2	51-52
i. Even though it was not identified or listed as a hazardous waste by EPA or by a state. . . .	Q9I %	53-55

(Number of Records Coded) QREC11

10. In the spaces provided below, list the EPA Hazardous Waste Numbers for all hazardous wastes actually generated at this installation during the 1981 calendar year. If wastes were generated in mixed form, list the EPA Waste Number for each of the component wastes in the mixture separately. [EPA WASTE CODES ARE LISTED IN APPENDIX A OF THE GENERAL INSTRUCTIONS]

NOTE: IF NO EPA WASTE NUMBER APPLIES TO A PARTICULAR WASTE THAT IS HANDLED AS HAZARDOUS, PLEASE USE THE SPACE PROVIDED TO DESCRIBE THE UNNUMBERED WASTE, INCLUDING ITS CHEMICAL AND PHYSICAL COMPOSITION AND THE PROCESS THROUGH WHICH IT WAS GENERATED (e.g., SPENT MINERAL SPIRITS IN CONCENTRATED SLUDGE, CADMIUM LADEN SLUDGE FROM WASTE WATER TREATMENT PROCESS, ETC.)

EPA WASTE CODES BEGINNING WITH THE LETTERS "K", "U" AND "P": [LIST WASTE CODES ONLY]

a. |__|__|__|__|	d. |__|__|__|__|	g. |__|__|__|__|	j. |__|__|__|__|	/56-71
b. |__|__|__|__|	e. |__|__|__|__|	h. |__|__|__|__|	k. |__|__|__|__|	/72-87
c. |__|__|__|__|	f. |__|__|__|__|	i. |__|__|__|__|	l. |__|__|__|__|	/88-103

EPA WASTE CODES BEGINNING WITH THE LETTERS "D" AND "F": [LIST WASTE CODES, AND A DESCRIPTION OF EACH WASTE, INCLUDING ITS CHEMICAL AND PHYSICAL COMPOSITION, AND THE PROCESS THROUGH WHICH IT WAS GENERATED] /03

m. |__|__|__|__|	Description: _____	/16-19
n. |__|__|__|__|	Description: _____	/20-23
o. |__|__|__|__|	Description: _____	/24-27
p. |__|__|__|__|	Description: _____	/28-31
q. |__|__|__|__|	Description: _____	/32-35
r. |__|__|__|__|	Description: _____	/36-39
s. |__|__|__|__|	Description: _____	/40-43
t. |__|__|__|__|	Description: _____	/44-47
u. |__|__|__|__|	Description: _____	/48-51
v. |__|__|__|__|	Description: _____	/52-55
w. |__|__|__|__|	Description: _____	/56-59
x. |__|__|__|__|	Description: _____	/60-63

DESCRIPTIONS OF UNNUMBERED WASTES:

/64-65

IF ADDITIONAL SPACE IS REQUIRED, PLEASE CHECK HERE ☐ AND USE THE ADDITIONAL SPACE PROVIDED FOR THIS QUESTION ON PAGE 23. Q BOX 10 /66

11. Did this installation ship hazardous waste off site for treatment, storage, and/or disposal during 1981? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 12] . . . . . Q 11 . . . 1

No [SKIP TO QUESTION 19]. 2

12. What was the total quantity of hazardous waste that was shipped off site for treatment, storage, and/or disposal during the 1981 calendar year?

QUANTITY SHIPPED OFF SITE: _____ Q 12

76-79

[CIRCLE ONE]:

Metric tonnes. . . . . Q 12 UC 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: _____ 04

13. Of the total quantity of hazardous waste shipped off site for treatment, storage, and/or disposal in 1981 (as specified in Question 12), what percentage was shipped to facilities owned by other firms?

IF NO HAZARDOUS WASTE WAS SHIPPED TO FACILITIES OWNED BY OTHER FIRMS DURING 1981, PLEASE CHECK HERE ☐ AND SKIP TO QUESTION 16. Q BOX 13

79

PERCENTAGE SHIPPED TO FACILITIES OWNED BY OTHER FIRMS: Q 13 %

80-82

14. During 1981, what was the cost incurred by this installation for transporting these hazardous wastes to facilities owned by other firms? [PLEASE INCLUDE THE COST OF LABOR AND MATERIALS FOR 1981, IF THIS INSTALLATION PROVIDED ITS OWN TRANSPORTATION SERVICES. IF TRANSPORTATION SERVICES WERE PROVIDED TO THIS INSTALLATION FOR A FEE, INCLUDE THE FEES PAID FOR SERVICES USED IN 1981.]

COST OF WASTE TRANSPORTATION SERVICES IN 1981:. . . . . $ Q 14

83-91

15. During 1981, what was this installation's total cost, including transportation costs reported in Question 14, for the treatment, storage, and/or disposal of these hazardous wastes at facilities owned by other firms? [PLEASE INCLUDE THE AMOUNT PAID TO FACILITIES FOR TREATMENT, STORAGE, AND/OR OR DISPOSAL SERVICES, AS WELL AS AMOUNTS PAID OR COSTS INCURRED FOR TRANSPORTATION]

TOTAL COST OF TREATMENT, STORAGE, AND/OR DISPOSAL BY FACILITIES OWNED BY OTHER FIRMS FOR 1981: . . $ Q15

/92-100

16. Of the total quantity of hazardous waste shipped off site for treatment, storage, and/or disposal in 1981 (as specified in Question 12), what percentage was shipped out of state?

PERCENTAGE SHIPPED OUT OF STATE: Q16 %

17. Please provide the EPA Identification Number for each off-site facility to which this installation shipped hazardous waste for treatment, storage, and/or disposal during the 1981 calendar year, and indicate the total quantity of hazardous waste shipped and the total number of manifested shipments sent to each facility during the 1981 calendar year. [PLEASE USE THE SAME UNIT OF MEASURE THROUGHOUT THE TABLE. REMEMBER TO CIRCLE UNIT CODE AT THE BOTTOM OF THE PAGE] /34

IF ADDITIONAL SPACE IS REQUIRED TO ANSWER THIS QUESTION, PLEASE CHECK HERE ☐ AND USE THE ADDITIONAL SPACE PROVIDED FOR THIS QUESTION ON PAGE 24. Q17BOX17 /16

FACILITY EPA IDENTIFICATION NUMBER	Total quantity of hazardous waste shipped to facility during 1981*	Total number of manifested shipments sent to facility during 1981	
a. Q17A1	Q17A2	Q17A3	/17-40
b. Q17B1	Q17B2	Q17B3	/41-64
c. Q17C1	Q17C2	Q17C3	/65-88
d. Q17D1	Q17D2	Q17D3	/89-112
e. Q17E1	Q17E2	Q17E3	/16-39
f. Q17F1	Q17F2	Q17F3	/40-63

/105

*[CIRCLE ONE]:

Metric tonnes. Q17.4C 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: _____ 04

/64-65

18. Please provide the EPA Identification Number for each transporter whose services were used by this installation for the transportation of hazardous waste off site during 1981. [IF THIS INSTALLATION PROVIDED SOME OR ALL OF ITS OWN TRANSPORTATION SERVICES, PLEASE INCLUDE THIS INSTALLATION'S EPA IDENTIFICATION NUMBER BELOW.]

IF ADDITIONAL SPACE IS REQUIRED TO ANSWER THIS QUESTION, PLEASE CHECK HERE ☐ AND USE THE ADDITIONAL SPACE PROVIDED FOR THIS QUESTION ON PAGE 24. Q Box 18	/66

Hazardous waste transporter identification numbers:

a. Q18A /67-78

b. Q18B /79-90

c. Q18C /91-102

d. Q18D /103-114

The following questions relate to the quantity of waste which is recycled beneficially rather than treated or disposed. This would include wastes which are used or reused, such as for raw materials in production processes; or reclaimed, such as solvent redistillation, scrap metal reclaimed by secondary smelter, or wastes which are blended to make fuels. Beneficial use also includes "wastes used in a manner constituting disposal" such as waste applied directly to the land as dust suppressants or as fertilizers.

19. Did this installation generate any hazardous waste that was used, reused, recycled, or reclaimed (either on site or off site) before 1981? [CIRCLE ONLY ONE CODE]

Yes . . . . . Q.19 . . . 1 /115

No 2

20. Will any hazardous waste generated at this installation be used, reused, recycled, or reclaimed (either on site or off site) after 1981? [CIRCLE ONLY ONE CODE]

Yes . . . . . Q.20 . . . 1 /116

No 2

21. Did this installation generate any hazardous waste that was used, reused, recycled, or reclaimed (either on site or off site) during 1981? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 22] . . . . . Q.21 . . . 1 /117

No [SKIP TO QUESTION 26] 2

*22. In the table below, please specify the total quantity of hazardous waste generated at this installation that was used, reused, recycled or reclaimed (either on site or off site) during 1981. Of this total, indicate the quantity that was recycled on site at this installation during 1981; the quantity that was shipped off site during 1981 for recycling at a facility owned by this firm; and the quantity that was shipped off site during 1981 for recycling at a facility owned by another firm. [ENTER QUANTITIES AND CIRCLE UNIT CODE. PLEASE USE THE SAME UNIT OF MEASURE THROUGHOUT THE TABLE]

06

	QUANTITY
a. Total quantity generated that was used, reused, recycled, or reclaimed during 1981 [THE TOTAL QUANTITY REPORTED ON THIS LINE SHOULD EQUAL THE SUM OF THE QUANTITIES ON LINES b, c, AND d BELOW].	Q22A
b. Quantity recycled on site during 1981	Q22B
c. Quantity shipped off site during 1981 for recycling at a facility owned by this firm	Q22C
d. Quantity shipped off site during 1981 for recycling at a facility owned by another firm.	Q22D

-2-

[CIRCLE ONE]:

Metric tonnes. Q22UC 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: _____ 04

*Please note that this question, and Questions 23 through 25, refer to waste that was recycled, or shipped off site for recycling, during 1981, regardless of the year in which it was generated. The total in Line A of Question 22 will not necessarily equal the quantity reported in Question 9, since Question 9 refers to the waste generated in 1981 that was/is destined for recycling (either on site or off site), regardless of the year in which it was recycled.

/54

23. Please complete the following table for the five hazardous wastes generated at this installation which were shipped off site in greatest volume for use, reuse, recycling, or reclamation during the 1981 calendar year. [REFER TO FACING PAGE FOR INSTRUCTIONS FOR COMPLETING EACH COLUMN OF THE TABLE]

/55

IF THIS INSTALLATION DID NOT SHIP ANY HAZARDOUS WASTES OFF SITE TO BE USED, REUSED, RECYCLED, OR RECLAIMED DURING 1981, CHECK HERE ☐ AND SKIP TO QUESTION 24. Q Box 23

# of manifests Z's Q.V.REC

waste order number Q23WN01 TO Q23WN1.

COLUMN A EPA number and description of wastes shipped off-site for use, reuse, recycling, or reclamation	COLUMN B EPA Identification Numbers of three facilities to which waste was sent in greatest volume for use, reuse, recycling, or reclamation.	COLUMN C Quantity of waste shipped to each facility during 1981*
a. Q23A01 Description: Q23A02 Q23A03	Q23B1A01 Q23B2A01 Q23BV01 Q23B1A02 Q23B2A02 Q23BV02 Q23B1A03 Q23B2A03 Q23BV03	Q23C01 Q23C02 Q23C03
b. Q23A04 Description: Q23A05 Q23A06	Q23B1A04 Q23B2A04 Q23BV04 Q23B1A05 Q23B2A05 Q23BV05 Q23B1A06 Q23B2A06 Q23BV06	Q23C04 Q23C05 Q23C06
c. Q23A07 Description: Q23A08 Q23A09	Q23B1A07 Q23B2A07 Q23BV07 Q23B1A08 Q23B2A08 Q23BV08 Q23B1A09 Q23B2A09 Q23BV09	Q23C07 Q23C08 Q23C09
d. Q23A10 Description: Q23A11 Q23A12	Q23B1A10 Q23B2A10 Q23BV10 Q23B1A11 Q23B2A11 Q23BV11 Q23B1A12 Q23B2A12 Q23BV12	Q23C10 Q23C11 Q23C12
e. Q23A13 Description: Q23A14 Q23A15	Q23B1A13 Q23B2A13 Q23BV13 Q23B1A14 Q23B2A14 Q23BV14 Q23B1A15 Q23B2A15 Q23BV15	Q23C13 Q23C14 Q23C15

*[CIRCLE ONE]:

Metric tonnes. 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: Q23C4C01 to Q23C4C15 04

COLUMN A: ENTER EPA WASTE NUMBERS AND SHORT DESCRIPTIONS OF THE FIVE WASTES INCLUDING DESCRIPTIONS OF THE PROCESSES THROUGH WHICH EACH WASTE WAS GENERATED. [EPA WASTE CODES ARE LISTED IN APPENDIX A OF THE GENERAL INSTRUCTIONS]

COLUMN B: ENTER THE EPA IDENTIFICATION NUMBERS OF THE THREE FACILITIES TO WHICH EACH WASTE WAS SHIPPED IN GREATEST VOLUME.

COLUMN C: INDICATE THE QUANTITY OF WASTE SHIPPPED TO EACH FACILITY AND CIRCLE THE UNIT CODE AT THE BOTTOM OF THE COLUMN. PLEASE USE THE SAME UNIT OF MEASURE FOR ALL WASTES IN THE TABLE.

COLUMN D: CIRCLE THE CODE OR CODES THAT INDICATE HOW EACH WASTE WAS STORED PRIOR TO SHIPMENT OFF SITE FOR USE, REUSE, RECYCLING, OR RECLAMATION.

COLUMN E: FOR EACH FACILITY, INDICATE THE AVERAGE NUMBER OF DAYS EACH WASTE WAS STORED PRIOR TO SHIPMENT OFF SITE FOR USE, REUSE, RECYCLING, OR RECLAMATION.

107R1

COLUMN D — How was waste stored prior to shipment off site for use, reuse, recycling, or reclamation? [CIRCLE ALL THAT APPLY FOR EACH FACILITY]						COLUMN E — Average number of days waste was stored prior to shipment off site for use, reuse, recycling, or reclamation.
In containers	In above ground tanks	In below ground tanks	In piles	In surface impoundments	Other [SPECIFY]:	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	
01	02	03	04	05	06	

(coding batch number) Q23C01 TO Q23C015

/50

24. Please complete the following table for the five hazardous wastes generated at this installation which were used, reused, recycled, or reclaimed on site in greatest volume during the 1981 calendar year. [REFER TO FACING PAGE FOR INSTRUCTIONS FOR COMPLETING EACH COLUMN OF THE TABLE]

IF THIS INSTALLATION DID NOT USE, REUSE, RECYCLE, OR RECLAIM ANY HAZARDOUS WASTES ON SITE IN 1981, CHECK HERE ☐ AND GO TO QUESTION 26. Q3-X24

/57

(Quantity Recycled) Q.VREC ?

COLUMN A	COLUMN B					COLUMN C
	How was this waste used, reused, recycled, or reclaimed on site? [CIRCLE ALL THAT APPLY]					
EPA Number and description of wastes used, reused, recycled or reclaimed on site	As feedstock in manufacturing process	As fuel or fuel supplement	In manner constituting disposal	Reclaimed	Other [SPECIFY]:	Quantity of waste used, reused, recycled or reclaimed during 1981*
a. |___|___|___|___| Description: Q24AA01	01 Q24B101	02 Q24B201	03 Q24B301	04 Q24B401	05 Q24B501	Q24C01
b. |___|___|___|___| Description: Q24AA02	01 Q24B102	02 Q24B202	03 Q24B302	04 Q24B402	05 Q24B502	Q24C02
c. |___|___|___|___| Description: Q24AA03	01 Q24B103	02 Q24B203	03 Q24B303	04 Q24B403	05 Q24B503	Q24C03
d. |___|___|___|___| Description: Q24AA04	01 Q24B104	02 Q24B204	03 Q24B304	04 Q24B404	05 Q24B504	Q24C04
e. |___|___|___|___| Description: Q24AA05	01 Q24B105	02 Q24B205	03 Q24B305	04 Q24B405	05 Q24B505	Q24C05

*[CIRCLE ONE]:

Metric tonnes. 01

English (or short) tons. 02

Gallons. 03

Other (specify). . . . . Q24C4C01 TO Q24C4C05

COLUMN A: ENTER EPA WASTE NUMBERS AND SHORT DESCRIPTIONS OF THE FIVE WASTES, INCLUDING DESCRIPTIONS OF THE PROCESSES THROUGH WHICH EACH WASTE WAS GENERATED. [EPA WASTE CODES ARE LISTED IN APPENDIX A OF THE GENERAL INSTRUCTIONS]

COLUMN B: CIRCLE THE CODE OR CODES THAT INDICATE HOW THE WASTE WAS USED, REUSED, RECYCLED OR RECLAIMED ON SITE.

COLUMN C: INDICATE THE QUANTITY OF WASTE USED, REUSED, RECYCLED OR RECLAIMED DURING 1981 AND CIRCLE THE UNIT CODE AT THE BOTTOM OF THE TABLE. PLEASE USE THE SAME UNIT OF MEASURE FOR ALL WASTES IN THE TABLE.

COLUMN D: CIRCLE THE CODE OR CODES THAT INDICATE HOW EACH WASTE WAS STORED AT THIS FACILITY PRIOR TO USE, REUSE, RECYCLING, OR RECLAMATION.

COLUMN E: INDICATE THE AVERAGE NUMBER OF DAYS EACH WASTE WAS STORED PRIOR TO USE, REUSE, RECYCLING, OR RECLAMATION.

[08R]

COLUMN D: How was waste stored prior to use, reuse, recycling, or reclamation? [CIRCLE ALL THAT APPLY]						COLUMN E: Average number of days waste was stored prior to use, reuse, recycling, or reclamation
In containers	In above ground tanks	In below ground tanks	In piles	In surface impoundments	Other [SPECIFY]:	
Q24D101 01	Q24D201 02	Q24D301 03	Q24D401 04	Q24D501 05	06 Q24D601	Q24E01 Days
Q24D102 01	Q24D202 02	Q24D302 03	Q24D402 04	Q24D502 05	06 Q24D602	Q24E02 Days
Q24D103 01	Q24D203 02	Q24D303 03	Q24D403 04	Q24D503 05	06 Q24D603	Q24E03 Days
Q24D104 01	Q24D204 02	Q24D304 03	Q24D404 04	Q24D504 05	06 Q24D604	Q24E04 Days
Q24D105 01	Q24D205 02	Q24D305 03	Q24D405 04	Q24D505 05	06 Q24D605	Q24E05 Days

(coding batch #) Q24C301 TO Q24C305

/09/

25. For each waste indicated in Question 24 as being used in a manner constituting disposal ("03" circled in Column B), please describe the specific manner in which the waste was used:

Q 25

/16-17

26. The RCRA regulations allow installations with tanks which are a part of a wastewater treatment system that is subject to regulation under the Clean Water Act, and which receive and treat or store wastewater which is hazardous, to operate these tanks without obtaining a permit or interim status. This exemption, which was issued on November 17, 1980, is called the wastewater treatment exemption. During 1981, were there any tanks at this installation which were being operated under the wastewater treatment exemption? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 27] . . . . . Q 26 . . 1

No [SKIP TO QUESTION 29]. 2

/18

27. During 1981, how many tanks at this installation were used for wastewater treatment under the wastewater treatment exemption?

NUMBER OF TANKS USED UNDER WASTEWATER TREATMENT EXEMPTION: Q 27

/19-21

28. What is the averace design capacity of a tank used for wastewater treatment during 1981? (That is, how much wastewater could the average wastewater treatment tank hold?) [ENTER QUANTITY AND CIRCLE UNIT CODE]

AVERAGE CAPACITY OF WASTEWATER TREATMENT TANK: Q 28

/22-30

[CIRCLE ONE]:

Metric tonnes . . . . . Q 28 M C . . 01

English (or short) tons 02

Gallons 03

Other [SPECIFY]:. 04

/31-32

29. The RCRA regulations allow waste generators to accumulate hazardous waste on site for up to 90 days without obtaining a permit or interim status, provided these generators accumulate waste in accordance with certain standards. This is called the 90-day rule. During 1981, were wastes accumulated at this installation under the 90-day rule? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 30]. . . . . Q29 . . 1

No [SKIP TO QUESTION 45] 2

Don't know [SKIP TO QUESTION 45). 8

/33

30. On an average day during 1981, how much accumulated (90-day rule) hazardous waste was being kept at this installation? [ENTER QUANTITY AND CIRCLE UNIT CODE]

QUANTITY OF ACCUMULATED WASTE KEPT ON SITE ON AVERAGE DAY: Q30

/34-

[CIRCLE ONE]:

Metric tonnes . . . . . Q30C4C . . 01

English (or short) tons 02

Gallons 03

Other [SPECIFY]: _____ 04

/43-44

31. During 1981, how many on-site areas did this installation have in which hazardous waste was accumulated under the 90-day rule?

NUMBER OF ON-SITE ACCUMULATION AREAS: Q31

/45-4

32. Please specify how many of the on-site hazardous waste accumulation areas were located:

	Number of Areas
a. Within the manufacturing or industrial area (i.e., at or near locations where hazardous wastes are generated). . .	Q32A
b. Adjacent to, or separate from, the manufacturing or industrial area (i.e., a loading dock, staging area, or other location outside of the generating area).	Q32B

/48-50

/51-5

33. Please specify how many of the on-site hazardous waste accumulation areas were supervised by personnel:

	Number of Areas	
a. With thorough knowledge of plant operations, including the process that produced the hazardous wastes, and knowledge of other hazardous materials, if present: . .	Q33A	/54-56
b. With knowledge of plant operations limited to the operation of the accumulation area (i.e., when and how to load and unload containers or transfer wastes into and out of the area):	Q33B	/57-59

34. Of the hazardous waste accumulated under the 90-day rule in 1981, what percentage was accumulated in:

	Percentage		
a. Tanks	Q34A	%	60-62
b. 55 gallon containers.	Q34B	%	/63-65
c. Other containers [SPECIFY TYPE AND CAPACITY]: ____	Q34C1		/66-67
_____	Q34C2	%	/68-70
TOTAL SHOULD EQUAL.	100 %		

35. During 1981, how many tanks at this installation were used for hazardous waste accumulation under the 90-day rule?

IF TANKS WERE NOT USED BY THIS INSTALLATION FOR HAZARDOUS WASTE ACCUMULATION UNDER THE 90-DAY RULE DURING 1981, CHECK HERE ☐ AND SKIP TO QUESTION 37. Q Box 35 /71

NUMBER OF TANKS USED FOR ACCUMULATION UNDER 90-DAY RULE: Q35 /72-74

36. What was the average design capacity of a tank used for hazardous waste accumulation under the 90-day rule during 1981? (That is, how much waste could the average accumulation tank hold?) [ENTER QUANTITY AND CIRCLE UNIT CODE]

AVERAGE CAPACITY OF WASTE ACCUMULATION TANK: Q36 /75-83

[CIRCLE ONE]

Metric tonnes Q36.4C. 01

English (or short) tons 02

Gallons 03

Other [SPECIFY]: _____ 04 /84-85

37. During 1981, how many areas were used for hazardous waste accumulation in containers under the 90-day rule?

IF CONTAINER ACCUMULATION AREAS WERE NOT USED BY THIS INSTALLATION FOR HAZARDOUS WASTE ACCUMULATION UNDER THE 90-DAY RULE DURING 1981, CHECK HERE ☐ AND SKIP TO QUESTION 39 Q38x37 /86

NUMBER OF CONTAINER ACCUMULATION AREAS: Q37 /87-89

38. What was the average quantity of hazardous waste held in container accumulation area(s) under the 90-day rule during 1981? [ENTER QUANTITY AND CIRCLE UNIT CODE]

AVERAGE QUANTITY BEING HELD IN CONTAINER ACCUMULATION AREAS: Q38 /90-98

[CIRCLE ONE]:

Metric tonnes Q38.4C. 01

English (or short) tons 02

Gallons 03

Other [SPECIFY]: _____ 04 /99-101

39. During 1981, was any of the accumulated (90-day rule) hazardous waste processed on site in any of the following ways? [CIRCLE ONE CODE FOR EACH PROCESS]

	YES	NO	
a. On-site treatment . . . . . Q39A. . .	1	2	/101
b. On-site disposal. . . . . Q39B. . .	1	2	/102
c. On-site use, reuse, recycling, or reclamation . . . . . Q39C.	1	2	/103
d. Other on-site process [SPECIFY]: Q3901 Q3902	1	2	/104

/105-106

40. During '981, was any of the accumulated (90-day rule) hazardous waste shipped to any off-site treatment, disposal or recycling facility? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 41]. . . . . Q.40 . 1

No [SKIP TO QUESTION 45] . . . . . 2 /107

Don't know [SKIP TO QUESTION 45]. 8

41. During 1981, how much waste constituted a normal load for shipping off site to a treatment, disposal or recycling facility? [ENTER QUANTITY AND CIRCLE UNIT CODE]

SIZE OF NORMAL LOAD: Q 41 /108-11

[CIRCLE ONE]:

Metric tonnes Q.41.CC 01

English (or short) tons 02

Gallons 03

Other [SPECIFY]: _____ 04

/117-11

42. What size waste shipment do you consider to be the optimum size for this installation? [ENTER QUANTITY AND CIRCLE UNIT CODE] |10|

SIZE OF OPTIMUM LOAD: Q 42 /16-2

[CIRCLE ONE]:

Metric tonnes Q.42.CC 01

English (or short) tons 02

Gallons 03

Other [SPECIFY]: _____ 04

/25-26

43. During 1981, at your normal operating rate, approximately how many days did it take to generate a waste shipment of the optimum size (as specified in Question 42)?

NUMBER OF DAYS TO GENERATE: Q 43 /27-29

44. During 1981, how often was it necessary to make an off-site shipment that was smaller than optimum (as specified in Question 42) in order to meet the special provisions of the 90-day rule? [ANSWER AS PERCENTAGE OF THE NUMBER OF 1981 WASTE SHIPMENTS]

PERCENTAGE OF WASTE SHIPMENTS SMALLER THAN OPTIMUM IN 1981: Q 44 % /30-

45. Waste exchange is the process whereby waste from an industry is used as raw material (or to treat waste) in another industry. Is this firm interested in participating in efforts by EPA or other organizations to facilitate the development of waste exchanges? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 46]. . . . . Q45 . . . 1

No [PLEASE SIGN THE CERTIFICATION STATEMENT ON PAGE 22 OF THIS QUESTIONNAIRE AND RETURN THIS FORM TO EPA] . . . . . 2 /33

46. OPTIONAL: Please list the Chemical Abstract Service Registry Number or Numbers for each waste generated at this installation during the 1981 calendar year.

NOTE: ALTHOUGH THIS QUESTION IS OPTIONAL, THE DATA OBTAINED FROM RESPONSES CAN BE USED BY INTERESTED PARTIES TO FACILITATE THE USE, REUSE, RECYCLING, OR RECLAMATION OF HAZARDOUS WASTES AND PERHAPS DIMINISH THE COMPLIANCE BURDEN IMPOSED BY RCRA. THIS DATA WILL BE USED BY EPA, STATES, PRIVATE ENTERPRISES, AND OTHERS WHO MAY HAVE AN INTEREST IN THE SOURCES OF INDUSTRIAL WASTE THAT MAY BE RECYCLABLE.

Chemical Abstract Service Registry Numbers:

Q46

PLEASE SIGN THE CERTIFICATION STATEMENT ON NEXT PAGE AND RETURN THIS QUESTIONNAIRE TO EPA

CERTIFICATION STATEMENT

THE GENERATOR OR HIS AUTHORIZED REPRESENTATIVE MUST SIGN AND DATE THE CERTIFICATION WHERE INDICATED. THE PRINTED OR TYPED NAME OF THE PERSON SIGNING THE CERTIFICATION MUST ALSO BE INCLUDED WHERE INDICATED.

CERTIFICATION:

I certify under penalty of law that I have personally examined and am familiar with the information submitted in this and all attached documents, and that based on my inquiry of those individuals immediately responsible for obtaining the information, I believe that the submitted information is true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment.

PRINT OR TYPE NAME	SIGNATURE	DATE SIGNED

AFTER COMPLETING THIS QUESTIONNAIRE, RETURN IT TO EPA IN THE ENVELOPE ENCLOSED IN THE QUESTIONNAIRE PACKAGE.

IF THIS FACILITY HAS RECEIVED MORE THAN ONE QUESTIONNAIRE, PLEASE RETURN ALL COMPLETED QUESTIONNAIRES IN THE SAME ENVELOPE.

TABLE A

CONTINUATION SHEET FOR QUESTION 10

EPA WASTE CODES BEGINNING WITH THE LETTERS "K," "U," AND "P": [LIST WASTE CODES ONLY]

a.	Q10AA01	TO12	d.	Q10DA01	TO12	g.	Q10GA01	TO12	j.	Q10JA01	TO12
b.	Q10BA01	TO12	e.	Q10EA01	TO12	h.	Q10HA01	TO12	k.	Q10KA01	TO12
c.	Q10CA01	TO12	f.	Q10FA01	TO12	i.	Q10IA01	TO12	l.	Q10LA01	TO12

EPA WASTE CODES BEGINNING WITH THE LETTERS "D" AND "F": [LIST WASTE CODES AND A DESCRIPTION OF EACH WASTE, INCLUDING ITS CHEMICAL AND PHYSICAL COMPOSITION, AND THE PROCESS THROUGH WHICH IT WAS GENERATED]

m.		Description:	Q10MA01 TO Q10MA12
n.		Description:	Q10NA01 TO Q10NA12
o.		Description:	Q10OA01 to Q10OA12
p.		Description:	Q10PA01 to Q10PA12
q.		Description:	Q10QA01 to Q10QA12
r.		Description:	Q10RA01 to Q10RA12
s.		Description:	Q10SA01 to Q10SA12
t.		Description:	Q10TA01 to Q10TA12
u.		Description:	Q10UA01 to Q10UA12
v.		Description:	Q10VA01 to Q10VA12
w.		Description:	Q10WA01 to Q10WA12
x.		Description:	Q10XA01 to Q10XA12

DESCRIPTIONS OF UNNUMBERED WASTES: Q10Y01 to Q10Y12

(number of wastes) QNW01 to QNW12

(coding batch #) Q10B1101 to Q10B1112

TABLE B

CONTINUATION SHEET FOR QUESTION 17

	FACILITY EPA IDENTIFICATION NUMBER	Total quantity of hazardous waste shipped to facility during 1981*	Total number of manifested shipments sent to facility during 1981	[12R]
1.	QBC1A101 QBC1A201 QBC1ANC1	QBC1BC1	QBC1CC1	/16-17 /18-21 /22-45
2.	QBC2A101 QBC2A201 QBC2ANC1	QBC2BC1	QBC2CC1	/46-69
3.	QBC3A101 QBC3A201 QBC3ANC1	QBC3BC1	QBC3CC1	/70-93
4.	QBC4A101 QBC4A201 QBC4ANC1	QBC4BC1	QBC4CC1	/94-11
5.	QBC1A102 QBC1A202 QBC1ANC2	QBC1BC2	QBC1CC2	/22-45
6.	QBC2A102 QBC2A202 QBC2ANC2	QBC2BC2	QBC2CC2	/46-69
7.	QBC3A102 QBC3A202 QBC3ANC2	QBC3BC2	QBC3CC2	/70-93
8.	QBC4A102 QBC4A202 QBC4ANC2	QBC4BC2	QBC4CC2	/94-11
9.	QBC1A103 QBC1A203 QBC1ANC3	QBC1BC3	QBC1CC3	/22-45
10.	QBC2A103 QBC2A203 QBC2ANC3	QBC2BC3	QBC2CC3	/46-69
11.	QBC3A103 QBC3A203 QBC3ANC3	QBC3BC3	QBC3CC3	/70-
12.	QBC4A103 QBC4A203 QBC4ANC3	QBC4BC3	QBC4CC3	/94-

TABLE C

CONTINUATION SHEET FOR QUESTION 18

[13R]

Hazardous waste transporter identification numbers:

a.	QTCAA101	QTCAA201	QTCANC1	/22-33
b.	QTCBA101	QTCBA201	QTCBNC1	/34-45
c.	QTCCA101	QTCCA201	QTCCNC1	/46-57
d.	QTCDA101	QTCDA201	QTCDNC1	/58-69
e.	QTCEA101	QTCEA201	QTCENC1	/70-81
f.	QTCFA101	QTCFA201	QTCFNC1	/82-93
g.	QTCAA102	QTCAA202	QTCANC2	/22-33
h.	QTCBA102	QTCBA202	QTCBNC2	/34-45
i.	QTCCA102	QTCCA202	QTCCNC2	/46-57
j.	QTCDA102	QTCDA202	QTCDNC2	/58-69
k.	QTCEA102	QTCEA202	QTCENC2	/70-81
l.	QTCFA102	QTCFA202	QTCFNC2	/82-93

OMB #: 2000-0424
Expires: December 31, 1992

U.S. ENVIRONMENTAL PROTECTION AGENCY
HAZARDOUS WASTE TREATMENT, STORAGE AND DISPOSAL
GENERAL QUESTIONNAIRE

PLEASE RECORD THE FOLLOWING INFORMATION, ONLY IF DIFFERENT FROM LABEL ABOVE.

Name of Facility: _____

Facility EPA
Identification Number: |__|__|__|__|__|__|__|__|__|__|__|__|

Mailing Address: _____
STREET OR P.O. BOX

_____
CITY STATE ZIP CODE

1. Please record the location of this facility.*

*PLEASE GIVE THE ACTUAL PHYSICAL LOCATION OF THE FACILITY CORRESPONDING TO THE EPA IDENTIFICATION NUMBER ABOVE, RATHER THAN ITS MAILING ADDRESS.

ADDRESS: _____

CITY: _____ COUNTY: Q1A /68-70

STATE: _____ ZIP CODE: Q1B /71-72

2. Whom should we contact for follow-up at this facility?

NAME: _____ Q2

TITLE: _____

PHONE NUMBER: |__|__|__| - |__|__|__| - |__|__|__|__| EXTENSION: |__|__|__|__|
AREA CODE

3. Please indicate the type(s) of hazardous waste activity(ies) in which this installation was engaged during the 1981 calendar year. [CIRCLE ALL CODES THAT APPLY]

a. Hazardous waste generation. .	Q3.A	01	73-74
b. Hazardous waste treatment . .	Q3.B	02	75-76
c. Hazardous waste storage . . .	Q3.C	03	77-78
d. Hazardous waste disposal. . .	Q3.D	04	79-80
e. Hazardous waste transportation.	Q3.E	05	81-82
f. Recycling of hazardous waste. .	Q3.F	06	83-84
g. None of the above	Q3.G	07	85-86

GO ON TO QUESTION 4

IF CODES "02", "03" AND/OR "04" ARE CIRCLED, PLEASE GO TO QUESTION 4.

IF YOU HAVE NOT CIRCLED CODES "02," "03" OR "04," PLEASE SIGN THE CERTIFICATION STATEMENT ON PAGE 37 AND RETURN THIS QUESTIONNAIRE TO EPA.

4. What was the year in which waste management operations first began at this facility? (That is, in what year was the original construction/development of the waste management operations completed?)

YEAR WASTE MANAGEMENT BEGAN: _____ C4 87-90

5. Please give the sizes of each of the following waste management areas at this facility. [ENTER SIZES AND CIRCLE UNIT CODE BELOW. PLEASE USE THE SAME UNIT OF MEASURE FOR THE ENTIRE TABLE] /102/

		Size of area	
a.	Landfill.	Q5A	/16-23
b.	Surface impoundments.	Q5B	/24-31
c.	Waste piles	Q5C	/32-39
d.	Incinerators.	Q5D	/40-47
e.	Land treatment, application, or farming	Q5E	/48-55
f.	Treatment tank areas.	Q5F	/56-63
g.	Container storage areas	Q5G	/64-71
h.	Storage tank areas.	Q5H	/72-79
i.	Underground injection wells (surface operation area only)	Q5I	/80-87
j.	Recycling	Q5J	/88-95
k.	Common waste management area.	Q5K	/96-103
l.	Other waste management operations	Q5L	/104-111
m.	TOTAL WASTE MANAGEMENT AREA AT FACILITY	Q5M	/112-119
n.	TOTAL AREA OF FACILITY.	Q5N	/120-127

[CIRCLE ONE]:

Square feet. . . . . Q5UC . . 01

Square yards 02

Acres. 03

Other [SPECIFY]: _____ 04

/128-129

(IF information not available separately for employees, give info. for entire facility) Q Box 6

5. Please complete the following table for the employees engaged in the waste management operations at this facility.

ON LINE 6a: Enter the usual number of employees from each of the occupation categories who are engaged in the waste management operations.

ON LINE 6b: Enter the average hourly wage of the employees within each occupational category who are engaged in waste management operations. [IF THIS INFORMATION IS NOT AVAILABLE SEPARATELY FOR WASTE MANAGEMENT EMPLOYEES, PLEASE CHECK HERE ___ AND GIVE THE INFORMATION, BY OCCUPATIONAL CATEGORY, FOR THE ENTIRE FACILITY]

ON LINES 6c THROUGH 6n: Indicate the total number of person-hours per week devoted to each of the listed operations by the waste management employees in each of the occupational categories. [FOR EXAMPLE, IF THREE LABORATORY WORKERS USUALLY SPEND TEN HOURS PER WEEK EACH ENGAGED IN ACTIVITIES RELATED TO THE LANDFILL OPERATION AT THIS FACILITY, ENTER "30" ON LINE 6c UNDER THE COLUMN LABELED "LABORATORY AND PROFESSIONALS"]

	Laboratory & professionals	Drivers & equipment operators	All other skilled employees	Non-skilled employees	TOTAL
6a. Number of employees engaged in waste management operations at this facility	Q6A1	Q6A2	Q6A3	Q6A4	Q6A5
6b. Average hourly wage for waste management employees in each occupational category	Q6B1	Q6B2	Q6B3	Q6B4	Q6B5
6c. Total person-hours per week in landfill operations	Q6C1	Q6C2	Q6C3	Q6C4	Q6C5
6d. Total person-hours per week in surface impoundment operations	Q6D1	Q6D2	Q6D3	Q6D4	Q6D5
6e. Total person-hours per week in waste piles operations	Q6E1	Q6E2	Q6E3	Q6E4	Q6E5
6f. Total person-hours per week in incinerator operations	Q6F1	Q6F2	Q6F3	Q6F4	Q6F5
6g. Total person-hours per week in land treatment (including land application, land farming) operations	Q6G1	Q6G2	Q6G3	Q6G4	Q6G5

	Laboratory & professionals	Drivers & equipment operators	All other skilled employees	Non-skilled employees	TOTAL	
6h. Total person-hours per week in <u>treatment tank</u> operations	Q6H1	Q6H2	Q6H3	Q6H4	Q6H5	/91-1
6i. Total person-hours per week in <u>container storage</u> operations	Q6I1	Q6I2	Q6I3	Q6I4	Q6I5	116-40
6j. Total person-hours per week in <u>storage tank</u> operations	Q6J1	Q6J2	Q6J3	Q6J4	Q6J5	41-65
6k. Total person-hours per week in <u>underground injection well</u> operations	Q6K1	Q6K2	Q6K3	Q6K4	Q6K5	66-90
6l. Total person-hours per week in <u>recycling</u> operations	Q6L1	Q6L2	Q6L3	Q6L4	Q6L5	91-115
6m. Total person-hours per week in <u>other waste management</u> operations	Q6M1	Q6M2	Q6M3	Q6M4	Q6M5	116-140
6n. Total person-hours per week in <u>ALL waste management</u> operations at this facility [TOTAL ON LINE 6n SHOULD EQUAL THE SUM OF LINES 6c THROUGH 6m]:	Q6N1	Q6N2	Q6N3	Q6N4	Q6N5	41-65

7. In the table below, please list the primary SIC (Standard Industrial Classification) code of this facility, and up to three secondary SIC codes, if more than one code is required to describe this facility. [IF YOU DO NOT KNOW THE SIC CODE(S) FOR THIS FACILITY, PLEASE SELECT THE MOST APPROPRIATE CODE(S) FROM APPENDIX C IN THE GENERAL INSTRUCTIONS]

a. Primary SIC code	9 7A	66-69
Secondary SIC codes [PLEASE LIST IN DESCENDING ORDER OF IMPORTANCE]:		
b.	9 7B	70-73
c.	0 7 C	74-77
d.	9 7 D	78-81

8. Please specify the ownership status of this facility. That is, is the facility owned by the federal government, a state government, a local government (such as a city, town, county or parish), or is it privately owned? [CIRCLE ONLY ONE CODE]

Solely owned by federal government 01
Solely owned by state government 02
Solely owned by local government 03
Privately owned. 04
Other [SPECIFY]: C S 05

82

9. Please specify the status of the operator of this facility. That is, is the facility operated by the federal government, a state government, a local government (such as a city, town, county, or parish), or is it privately operated? [CIRCLE ONLY ONE CODE]

Solely operated by federal government 01
Solely operated by state government 02
Solely operated by local government. 03
Privately operated 04
Other [SPECIFY]: C O 05

84-85

10. What was the total quantity of waste (both hazardous and nonhazardous) that this facility treated, stored or disposed on this site during 1981? [ENTER QUANTITY AND CIRCLE UNIT CODE]

> NOTE: WHAT IS DESIRED HERE IS THE QUANTITY OF WASTE THAT "CAME THROUGH THE FRONT DOOR," OR ENTERED THE FACILITY'S TREATMENT, STORAGE, OR DISPOSAL OPERATIONS, IN 1981, COUNTING ONLY ONCE ANY QUANTITIES OF WASTES OR WASTE MIXTURES THAT WERE REPROCESSED THROUGH MULTIPLE TECHNOLOGIES, OR TREATMENT, STORAGE, OR DISPOSAL CHAINS.

QUANTITY OF WASTE HANDLED: 0 /0 /36-94

[CIRCLE ONE]:

Metric tonnes. 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: 0 / 0 / 0 04 /37-38

11. What was the total quantity of waste (both hazardous and nonhazardous) that this facility could have treated, stored or disposed on site during 1981, if the facility had been operating at full capacity the whole year? [SEE NOTE TO QUESTION 10. ENTER QUANTITY AND CIRCLE UNIT CODE]

QUANTITY THAT COULD HAVE BEEN HANDLED: 0 / / /39-46

[CIRCLE ONE]:

Metric tonnes. 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: 0 / / / 0 04 /47-48

12. What was the total quantity of hazardous waste that this facility treated, stored or disposed on site during 1981? [SEE NOTE TO QUESTION 10. ENTER QUANTITY AND CIRCLE UNIT CODE]

QUANTITY OF HAZARDOUS WASTE HANDLED: C 12 /108-116

[CIRCLE ONE]:

Metric tonnes. 01
English (or short) tons. 02
Gallons. 03
Other [SPECIFY]: C 12 U C 04 /117-118

13. What was the total quantity of hazardous waste that this facility could have treated, stored or disposed on site during 1981, if the facility had been operating at full capacity the whole year? [SEE NOTE TO QUESTION 10. ENTER QUANTITY AND CIRCLE UNIT CODE]

QUANTITY OF HAZARDOUS WASTE THAT COULD HAVE BEEN HANDLED: C 13 /119-127

[CIRCLE ONE]:

Metric tonnes. 01
English (or short) tons. 02
Gallons. 03
Other [SPECIFY]: C 13 U C 04 /128-129

14. During 1981, what percentage of the hazardous waste (specified in Question 12) entered into the treatment, storage and/or disposal operation by: /07/

	Percent	
a. Containers.	C 14 A	% /16-18
b. Tank trucks	C 14 B	% /19-21
c. Dump trucks	C 14 C	% /22-24
d. Railroad cars	C 14 D	% /25-27
e. Pipeline.	C 14 E	% /28-30
f. Other [SPECIFY]: _____	C 14 F,	% /31-33
_____	C 14 F 2	
TOTAL SHOULD EQUAL	100	% /34-36

15. Please provide the following information in the table below.

LINE A: Enter the quantities of wastes (both hazardous and nonhazardous) that were disposed of, treated, and/or stored, at the facility during 1981: [SEE NOTE BELOW]

LINE B: Enter the quantities of wastes (both hazardous and nonhazardous) that could have been disposed of, treated, and/or stored, at the facility during 1981, if the facility had been operating at full capacity the whole year; [SEE NOTE BELOW]

LINE C: Enter the quantities of hazardous wastes that were disposed of, treated, and/or stored, at the facility during 1981; [SEE NOTE BELOW]

LINE D: Enter the quantities of hazardous wastes that could have been disposed of, treated, and/or stored, at the facility during 1981, if the facility had been operating at full capacity the whole year. [SEE NOTE BELOW]

ENTER QUANTITIES ON THE TABLE BELOW AND CIRCLE THE UNIT CODE BELOW THE TABLE. PLEASE USE THE SAME UNIT OF MEASURE FOR ALL ANSWERS ON THE TABLE.

NOTE: TOTALS IN LINES A THROUGH D MAY EQUAL OR EXCEED ASSOCIATED TOTAL QUANTITIES PROVIDED IN QUESTIONS 10, 11, 12 AND 13, DUE TO MULTIPLE PROCESSING OF INDIVIDUAL WASTES OR WASTE MIXTURES. WHAT IS DESIRED HERE IS THE TOTAL QUANTITY OF WASTE THAT WAS INPUT, OR COULD BE INPUT, TO EACH PROCESS DURING 1981, REGARDLESS OF WHATEVER OTHER PROCESSES MAY HAVE BEEN APPLIED PREVIOUSLY OR SUBSEQUENTLY TO THE SAME WASTE, OR PORTIONS THEREOF.

	Finally disposed of at facility[1] — Did not dispose in 1981	Treated at facility[2] — Did not treat in 1981	Stored at facility[3] — Did not store in 1981	
	Q15A1	Q15A2	Q15A3	36-38
a. Quantities of wastes that were:	Q15A1	Q15A2	Q15A3	39-41
b. Quantities of wastes that could have been:	Q15B1	Q15B2	Q15B3	60-62
c. Quantities of hazardous wastes that were:	Q15C1	Q15C2	Q15C3	93-119
d. Quantities of hazardous wastes that could have been:	Q15D1	Q15D2	Q15D3	1081 16-42

[CIRCLE ONE]:

Metric tonnes. 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: Q15UC 04 43-44

[1] Include quantities disposed via: landfill, land application (land treatment, land farming), disposal surface impoundments, underground injection wells, ocean disposal, other disposal processes.

[2] Include quantities chemically, physically, biologically, or thermally treated in: tanks, treatment surface impoundments, incinerators, other treatment processes.

[3] Include quantities stored in: containers, tanks, waste piles, storage surface impoundments, other storage processes.

16. In the table below, please indicate which waste processing technologies were operating at this facility during 1981. [CIRCLE ONE CODE FOR EACH TECHNOLOGY]

Circle code 1 if the technology was in existence at the facility during 1981, was operational during 1981, and processed hazardous waste during 1981;

Circle code 2 if the technology was in existence at the facility during 1981, was operational during 1981, but did not process hazardous waste during 1981;

Circle code 3 if the technology was in existence at the facility during 1981, but was not operational during 1981;

Circle code 4 if the technology was under construction at the facility during 1981.

Circle code 5 if the technology was not in existence and not under construction at the facility during 1981.

Waste processing technology	In existence, operational, processed hazardous waste in 1981	In existence, operational, did not process hazardous waste in 1981	In existence, not operational in 1981	Under construction in 1981	Not in existence in 1981	
a. Underground injection well C16A	1	2	3	4	5	/46
b. Landfill C16B	1	2	3	4	5	/47
c. Land application area C16C	1	2	3	4	5	/47
d. Ocean disposal C16D	1	2	3	4	5	/48
e. Disposal surface impoundment C16E	1	2	3	4	5	/49
f. Treatment tanks C16F	1	2	3	4	5	50
g. Treatment surface impoundment C16G	1	2	3	4	5	/51
h. Incinerator C16H	1	2	3	4	5	/52
i. Storage containers C16I	1	2	3	4	5	/53
j. Storage tanks C16J	1	2	3	4	5	/54
k. Waste piles C16K	1	2	3	4	5	/55
l. Storage surface impoundment C16L	1	2	3	4	5	/56
m. Other [SPECIFY]: C16M1 C16M2	1	2	3	4	5	/57 /58-59

17. Please complete the following table for the ten hazardous wastes handled in largest volume by this facility in 1981. [PLEASE RECORD THE EPA WASTE NUMBERS OF WASTES HANDLED, BEGINNING WITH THE LARGEST VOLUME WASTE, IN THE COLUMNS ACROSS THE TOP OF THE TABLE.* A LIST OF EPA WASTE CODES IS INCLUDED IN THE GENERAL INSTRUCTIONS AS APPENDIX A.]

EPA WASTE NUMBER: AND DESCRIPTION OF WASTE:	Q17WN1	Q17WN2	Q17WN3
17a. What was the total quantity of this waste that was handled by this facility during 1981? [ENTER QUANTITY AND CIRCLE UNIT CODE FOR EACH WASTE]			
QUANTITY HANDLED IN 1981:	Q17A1	Q17A2	Q17A3
[CIRCLE ONE]:			
Metric tonnes	01	01	01
English (or short) tons. .	02	02	02
Gallons	03	03	03
Other [SPECIFY]:.	04	04	04
	Q17A11	Q17A12	Q17A13
17b. Was this waste stored at this facility? [CIRCLE ONLY ONE CODE]	Q17B1	Q17B2	Q17B3
Yes [GO TO QUESTION 17c] . . .	1	1	1
No [SKIP TO QUESTION 17e FOR THIS WASTE].	2	2	2
17c. What was the total quantity that entered storage in 1981? [ENTER QUANTITY AND CIRCLE UNIT CODE]			
--- TOTAL QUANTITY STORED . .	Q17C1	Q17C2	Q17C3
[CIRCLE ONE]:			
Metric tonnes	01	01	01
English (or short) tons .	02	02	02
Gallons	03	03	03
Other [SPECIFY]:.	04	04	04
	Q17C11	Q17C12	Q17C13

Q17WN4	Q17WN5	Q17WN6	Q17WN7	Q17WN8	Q17WN9	Q17WN10	60-99
_____	_____	_____	_____	_____	_____	_____	
_____	_____	_____	_____	_____	_____	_____	
_____	_____	_____	_____	_____	_____	_____	
Q17A4	Q17A5	Q17A6	Q17A7	Q17A8	Q17A9	Q17A10	16-35
01	01	01	01	01	01	01	
02	02	02	02	02	02	02	
03	03	03	03	03	03	03	
04	04	04	04	04	04	04	
Q17A14	Q17A15	Q17A16	Q17A17	Q17A18	Q17A19	Q17A20	36-55
Q17B4	Q17B5	Q17B6	Q17B7	Q17B8	Q17B9	Q17B10	
1	1	1	1	1	1	1	
2	2	2	2	2	2	2	16-35
Q17C4	Q17C5	Q17C6	Q17C7	Q17C8	Q17C9	Q17C10	36-
01	01	01	01	01	01	01	
02	02	02	02	02	02	02	
03	03	03	03	03	03	03	
04	04	04	04	04	04	04	
Q17C14	Q17C15	Q17C16	Q17C17	Q17C18	Q17C19	Q17C20	16-35

QUESTION 17 IS CONTINUED ON THE NEXT PAGE.

EPA WASTE NUMBER:	____	____	____
17d. What was the storage method for this waste? [CIRCLE ONLY ONE CODE. IF MORE THAN ONE METHOD WAS USED FOR A SINGLE WASTE TYPE, CIRCLE CODE "05" AND SPECIFY CODES "01" THROUGH "04," CORRESPONDING TO THE METHODS USED, IN ORDER FROM THE MOST PREVALENTLY USED METHOD TO THE LEAST]			
Storage in tanks	01	01	01
Storage in containers. . .	02	02	02
Storage in surface impoundments	03	03	03
Storage in waste piles . .	04	04	04
Other [SPECIFY]:	05	05	05
	Q17D1	Q17D2	Q17D3
17e. Was this waste treated at this facility? [CIRCLE ONLY ONE CODE]	Q17E1	Q17E2	Q17E3
Yes [GO TO QUESTION 17f] . .	1	1	1
No [SKIP TO QUESTION 17h FOR THIS WASTE].	2	2	2
17f. What was the total quantity treated in 1981? [DO NOT "DOUBLE COUNT" AMOUNTS OF A SINGLE WASTE THAT WERE PUT THROUGH MULTIPLE TREATMENT PROCESSES. ENTER QUANTITY AND CIRCLE UNIT CODE]			
TOTAL QUANTITY TREATED	Q17F1	Q17F2	Q17F3
[CIRCLE ONE]:			
Metric tonnes. . . .	01	01	01
English (or short) tons. . . .	02	02	02
Gallons.	03	03	03
Other [SPECIFY]: . .	04	04	04
	Q17F11	Q17F12	Q17F13

01	01	01	01	01	01	01
02	02	02	02	02	02	02
03	03	03	03	03	03	03
04	04	04	04	04	04	04
05	05	05	05	05	05	05
Q17D4	Q17D5	Q17D6	Q17D7	Q17D8	Q17D9	Q17D0
Q17E4	Q17E5	Q17E6	Q17E7	Q17E8	Q17E9	Q17E0
1	1	1	1	1	1	1
2	2	2	2	2	2	2
Q17F4	Q17F5	Q17F6	Q17F7	Q17F8	Q17F9	Q17F0
01	01	01	01	01	01	01
02	02	02	02	02	02	02
03	03	03	03	03	03	03
04	04	04	04	04	04	04
Q17G4	Q17G5	Q17G6	Q17G7	Q17G8	Q17G9	Q17G0

QUESTION 17 IS CONTINUED ON THE NEXT PAGE.

	EPA WASTE NUMBER:	____	____	____
17g.	What treatment process was used for this waste? [CIRCLE ONLY ONE CODE. IF MORE THAN ONE METHOD WAS USED FOR A SINGLE WASTE TYPE, CIRCLE CODE "04" AND SPECIFY CODES "01" THROUGH "03," CORRESPONDING TO THE METHODS USED, IN ORDER FROM THE MOST PREVALENTLY USED METHOD TO THE LEAST]			
	Treatment in tank(s) . . .	01	01	01
	Treatment in surface impoundment(s)	02	02	02
	Treatment by incineration	03	03	03
	Other [SPECIFY]:	04	04	04
		Q17G1	Q17G2	Q17G3
17h.	Was this waste disposed at this facility? [CIRCLE ONLY ONE CODE]	Q17H1	Q17H2	Q17H3
	Yes [GO TO QUESTION 17i]. . . .	1	1	1
	No [SKIP QUESTIONS 17i AND 17j FOR THIS WASTE]	2	2	2
17i.	What was the total quantity disposed in 1981? [ENTER QUANTITY AND CIRCLE UNIT CODE]			
	TOTAL QUANTITY DISPOSED:	Q17I1	Q17I2	Q17I3
	[CIRCLE ONE]:			
	Gallons.	01	01	01
	English (or short) tons	02	02	02
	Metric tonnes.	03	03	03
	Other [SPECIFY]:	04	04	04
		Q17-11	Q17-12	Q17-13

01	01	01	01	01	01	01
02	02	02	02	02	02	02
03	03	03	03	03	03	03
04	04	04	04	04	04	04
Q174	Q175	Q176	Q177	Q178	Q179	
Q174	Q175	Q176	Q177	Q178	Q179	
1	1	1	1	1	1	
2	2	2	2	2	2	
01	01	01	01	01	01	01
02	02	02	02	02	02	02
03	03	03	03	03	03	03
04	04	04	04	04	04	04
Q174	Q175	Q176	Q177	Q178	Q179	

QUESTION 17 IS CONTINUED ON THE NEXT PAGE.

	EPA WASTE NUMBER:	_____	_____	_____
17j.	What disposal process was used for this waste? [CIRCLE ONLY ONE CODE. IF MORE THAN ONE METHOD WAS USED FOR A SINGLE WASTE TYPE, CIRCLE CODE "05" AND SPECIFY CODES "01" THROUGH "04," CORRESPONDING TO THE METHODS USED, IN ORDER FROM THE MOST PREVALENTLY USED METHOD TO THE LEAST]			
	Disposal in injection wells.	01	01	01
	Disposal in landfill . . .	02	02	02
	Disposal in surface impoundments	03	03	03
	Disposal by land application.	04	04	04
	Other [SPECIFY]:	05	05	05
		017J1	017J2	017J3

01	01	01	01	01	01	01
02	02	02	02	02	02	02
03	03	03	03	03	03	03
04	04	04	04	04	04	04
05	05	05	05	05	05	05
UNIT4	UNIT5	UNIT6	UNIT7	UNIT8	UNIT9	UNIT10

(15)

(16-)

18. During 1981, did this facility receive any hazardous waste for treatment, storage or disposal that was generated off site? [CIRCLE ONLY ONE CODE]

Yes [GO TO QUESTION 19]. . . . . Q18 . . . . 1 /36

No [SKIP TO QUESTION 25]. 2

19. What was the total quantity of hazardous waste received for treatment, storage or disposal by this facility from off-site sources during 1981? [ENTER QUANTITY AND CIRCLE UNIT CODE]

QUANTITY FROM OFF-SITE SOURCES: Q19 /37-44

[CIRCLE ONE]:

Metric tonnes. 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: Q19C 04

20. What percentage of this quantity of hazardous waste (as specified in Question 19) was received in:

a. Containers. . . . . Q20A % /48-50

b. Tank trucks . . . . . Q20B % /51-53

c. Dump trucks . . . . . Q20C % 54-56

d. Railroad cars . . . . . Q20D % /57-59

e. Pipeline. . . . . Q20E % /60-62

f. Other [SPECIFY]: Q20F1 % /63-65

Q20F2

TOTAL SHOULD EQUAL 100 % /66-67

21. What percentage of this quantity of hazardous waste (as specified in Question 19) came from sources owned by other firms?

PERCENT FROM SOURCES OWNED BY OTHER FIRMS: Q21 % /68-70

22. What percentage of this quantity of hazardous waste (as specified in Question 19) came from small generators who are subject to the special provisions under RCRA?

PERCENT FROM SMALL GENERATORS: Q22 ____ %

23. In Column A of the table below, list the SIC codes of the five industries from which this facility received the greatest quantity of hazardous waste for treatment, storage or disposal in 1981. [IF YOU DO NOT KNOW THE SIC CODES OF THESE INDUSTRIES, PLEASE SELECT THE APPROPRIATE CODES FROM APPENDIX C IN THE GENERAL INSTRUCTIONS.]

In Column B, indicate the percent of the total amount of hazardous waste received from off-site sources (specified in Question 19) that was received from each of the five industries.

	COLUMN A SIC codes of five largest generators	COLUMN B Percent of total hazardous waste received
a.	Q23A1	Q23A2 ____ %
b.	Q23B1	Q23B2 ____ %
c.	Q23C1	Q23C2 ____ %
d.	Q23D1	Q23D2 ____ %
e.	Q23E1	Q23E2 ____ %

24. How was the hazardous waste content of waste shipments received by this facility during 1981 determined? Please specify the percentage of shipments for which:

a. Laboratory analyses were performed by this facility . . . . . Q24A ____ %

b. Documentation of waste characteristics was provided by the off-site source . . . . . Q24B ____ %

c. Documentation of waste characteristics was taken from data on similar wastes . . . . . Q24C ____ %

d. Other [SPECIFY]: ____ Q24D1 ____ %

____ Q24D2

II. GROUNDWATER MONITORING

/15/

25. Please indicate whether this facility has ever used or currently uses any of the following methods to prevent contamination of the aquifers or groundwater. For each method used, indicate the year and cost of installation. [CIRCLE ONE CODE FOR EACH METHOD, AND ENTER YEAR AND COST WHERE APPLICABLE]

	Yes	No	Year started	Cost	
a. Slurry wall	Q25A1 1	2	Q25A2	$ Q25A3	/16-29
b. Counterpumping.	Q25B1 1	2	Q25B2	$ Q25B3	/30-43
c. Other [SPECIFY]: _____	Q25C1 1	2	Q25C2	$ Q25C3	/44-57
Number of other methods specified Q25C4					
_____					/58-59

26. Does this facility have groundwater monitoring wells? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 27] . . . . . Q26 . . . 1 /60

No [SKIP TO QUESTION 29]. 2

27. How many hydraulically upgradient, and how many hydraulically downgradient wells for groundwater monitoring does this facility have?

a. NUMBER OF UPGRADIENT WELLS. . . . . Q27A /61-62

b. NUMBER OF DOWNGRADIENT WELLS. . . . . Q27B /63-64

28. Please describe up to six of this facility's groundwater monitoring wells, giving the specifications for at least one hydraulically upgradient well, and at least three hydraulically downgradient wells which are used to comply with the groundwater monitoring standards.

	Well 1	Well 2	Well 3	Well 4	Well 5	Well 6	
a. Is this an upgradient or downgradient well? [CIRCLE ONLY ONE CODE]	Q28A1	Q28A2	Q28A3	Q28A4	Q28A5	Q28A6	
Upgradient	1	1	1	1	1	1	/65-70
Downgradient	2	2	2	2	2	2	
b. What is the depth of this well in feet?							
DEPTH.	Q28B1 (FEET)	Q28B2 (FEET)	Q28B3 (FEET)	Q28B4 (FEET)	Q28B5 (FEET)	Q28B6 (FEET)	/71-74
c. What was the approximate cost of installing this well? [INCLUDE LABOR, MATERIALS AND FEES]							
INSTALLATION COST.	$Q28C1	$Q28C2	$Q28C3	$Q28C4	$Q28C5	$Q28C6	/75-79
d. In what year was this well installed?							
YEAR INSTALLED . . .	Q28D1 (YEAR)	Q28D2 (YEAR)	Q28D3 (YEAR)	Q28D4 (YEAR)	Q28D5 (YEAR)	Q28D6 (YEAR)	/80-83
e. How frequently are samples from this well drawn and analyzed? [ENTER FREQUENCY AND CIRCLE TIME UNIT CODE]							
FREQUENCY:	Q28E1	Q28E2	Q28E3	Q28E4	Q28E5	Q28E6	/84-111
[CIRCLE ONE]:							
Per month.	01	01	01	01	01	01	
Per year	02	02	02	02	02	02	
Other [SPECIFY]: .	03	03	03	03	03	03	
	Q28E14	Q28E24	Q28E34	Q28E44	Q28E54	Q28E64	/112-

29. Are there any geologic/hydrogeologic studies of this facility? [CIRCLE ONLY ONE CODE]

Q29

Yes . . . . . 1 /124

No. 2

III. SITE GEOGRAPHY

30. Is this facility located within one mile of a fault that has had displacement within the past 10,000 years (Holocene time)? [CIRCLE ONLY ONE CODE]

Q30

Yes [GO ON TO QUESTION 31]. . . . . 1 /125

No [SKIP TO QUESTION 37] 2

Don't know [SKIP TO QUESTION 37]. 8

31. How close is this facility to the fault?

DISTANCE FROM FAULT: Q31 feet /126-129

32. Has this facility experienced any seismic ground motion activity (e.g., subsidence, shaking, dislocacement) since its construction? [CIRCLE ONLY ONE CODE] [18]

Q32

Yes [GO ON TO QUESTION 33].	1
No [SKIP TO QUESTION 37]	2 /16
Don't know [SKIP TO QUESTION 37].	8

33. What type of seismic ground motion has this facility experienced? [CIRCLE ONE CODE FOR EACH ITEM]

	Yes	No	
a. Ground failure (liquifaction or slope stability). Q33A	1	2	/17
b. Earthquakes (snaking). Q33B	1	2	/18
c. Fault displacement Q33C	1	2	/19
d. Ground subsidence. Q33D	1	2	/20
e. Other [SPECIFY]: _____ Q33E1	1	2	/21
_____ Q33E2			/22-23

34. What was the intensity of the most severe seismic event experienced by this facility as measured by the Richter Magnitude Scale? [CIRCLE ONLY ONE CODE]

Q34

Less than 2 on the Richter scale.	01
From 2 up to 4 on the Richter scale	02
From 4 up to 6 on the Richter scale	03
From 6 up to 8 on the Richter scale	04
8 or greater on the Richter scale	05
Don't know.	98 /24-25

35. Did any seismic ground motion event ever damage any portion of this facility? [CIRCLE ONLY ONE CODE]

Q35

Yes	1 /26
No.	2

36. Has this facility incorporated any of the following design or locational criteria to mitigate the severity of ground motion induced damages? [CIRCLE ONE CODE FOR EACH ITEM]

	Yes	No	
a. Structural reinforcement . . . Q36.A . . .	1	2	/27
b. Site analysis (geologic) . . . Q36.B . .	1	2	/28
c. Construction materials . . . . Q36.C . .	1	2	/29
d. Structural design magnitude. . . Q36D . .	1	2	/30
e. Other [SPECIFY]: Q36E1	1	2	/31
Q36E2			/32-33

37. Is this facility, or a portion of this facility, located in a floodplain? [CIRCLE ONLY ONE CODE]

Q37

Yes [GO ON TO QUESTION 38]. 1

No [SKIP TO QUESTION 40] . . . . . 2 /34

Don't know [SKIP TO QUESTION 40]. 8

38. Which of the following best describes the floodplain on which this facility is located? [CIRCLE ONLY ONE CODE]

Q38

Riverine. 01

Coastal 02

Other [SPECIFY]: _____ 03

_____ /35-36

39. Which of the following best describes the frequency of flooding of the floodplain on which this facility is located? [CIRCLE ONLY ONE CODE]

Q39

Floods annually 01

Ten year floodplain 02

Fifty year floodplain 03

One hundred year floodplain 04

Five hundred year floodplain. 05

Other [SPECIFY]: _____ 06

_____ /37-38

40. Has this facility ever been flooded? [CIRCLE ONLY ONE CODE]

Q40

Yes [GO ON TO QUESTION 41] . . . . . 1 /39

No [SKIP TO QUESTION 43]. 2

41. What was the magnitude of the most severe flood experienced by this facility? [CIRCLE ONLY ONE CODE]

Q41

A 50 year flood	01	
A 100 year flood	02	
A 500 year flood	03	
Other [SPECIFY]: _____	04	
Don't know	98	/40-41

42. Has hazardous waste ever been released from this facility as a result of a flood? [CIRCLE ONLY ONE CODE]

Q42

Yes	1	
No	2	/42
Don't know	8	

43. What types of flood protection does this facility currently have in place? [CIRCLE ONE CODE FOR EACH TYPE OF PROTECTION]

IF THIS FACILITY DOES NOT CURRENTLY HAVE FLOOD PROTECTION, CHECK HERE ☐ AND SKIP TO QUESTION 45. Q80X43

/43

		Yes	No	
a. Levee	Q43A	1	2	/44
b. Elevation	Q43B	1	2	/45
c. Structural reinforcement	Q43C	1	2	/46
d. Warning system (waste removal prior to flood)	Q43D	1	2	/47
e. Other [SPECIFY]: _____	Q43E1	1	2	/48
_____	Q43E2			/49-50

44. Why was the flood protection instituted at this installation? [CIRCLE ONE CODE FOR EACH REASON]

		Yes	No	
a. RCRA	Q44A	1	2	/51
b. Local regulation	Q44B	1	2	/52
c. State regulation	Q44C	1	2	/53
d. Insurance requirements	Q44D	1	2	/54
e. Self-protection	Q44E	1	2	/55
f. Other [SPECIFY]:	Q44F1	1	2	/56
	Q44F2			/57-58

The following questions relate to the quantity of waste which is recycled rather than discarded. This would include wastes which are used or reused, as for raw materials in production processes; or recycled or reclaimed, such as solvent redistillation, scrap metal reclaimed by secondary smelter, or wastes which are blended to make fuels. Beneficial use also includes "wastes used in a manner constituting disposal" such as waste applied directly to the land as dust suppressants or as fertilizers.

45. Did this facility generate or receive any hazardous waste that was used, reused, recycled, or reclaimed (either on site or off site) before 1981? [CIRCLE ONLY ONE CODE]

Yes	Q45	1
No		2

/59

46. Will any hazardous waste generated or received by this facility be used, reused, recycled, or reclaimed (either on site or off site) after 1981? [CIRCLE ONLY ONE CODE]

Yes	Q46	1
No		2

/60

47. Did this facility generate or receive hazardous wastes that were used, reused, recycled, or reclaimed (either on site or off site) during 1981? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 48]	Q47	1
No [SKIP TO QUESTION 52]		2

/61

48. In the table below, please specify the total quantity of hazardous waste generated or received at this facility that was used, reused, recycled or reclaimed (either on site or off site) during 1981. Of this total, indicate the quantity that was recycled on site at this facility during 1981; the quantity that was shipped off site during 1981 for recycling at a facility owned by this firm; and the quantity that was shipped off site during 1981 for recycling at a facility owned by another firm. [ENTER QUANTITIES AND CIRCLE UNIT CODE. PLEASE USE THE SAME UNIT OF MEASURE THROUGHOUT THE TABLE]

	QUANTITY	
a. Total quantity generated or received that was used, reused, recycled, or reclaimed during 1981 [THE TOTAL QUANTITY REPORTED ON THIS LINE SHOULD EQUAL THE SUM OF THE QUANTITIES ON LINES b, c, AND d BELOW].	Q48A	/62-70
b. Quantity recycled on site during 1981	Q48B	/71-79
c. Quantity shipped off site during 1981 for recycling at a facility owned by this firm	Q48C	/80-
d. Quantity shipped off site during 1981 for recycling at a facility owned by another firm.	Q48D	/89-

[CIRCLE ONE]:

Metric tonnes. 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: Q48UC 04

/98-99

49. Please complete the following table for the five principal hazardous wastes generated or received by this facility which were shipped off site in greatest volume for use, reuse, recycling or reclamation during the 1981 calendar year. [REFER TO FACING PAGE FOR INSTRUCTIONS FOR COMPLETING EACH COLUMN OF THE TABLE]

IF THIS FACILITY DID NOT SHIP ANY HAZARDOUS WASTES OFF SITE TO BE USED, REUSED, RECYCLED OR RECLAIMED DURING 1981, CHECK HERE ☐ AND SKIP TO QUESTION 50. Q BOX 49

/100

(waste order number) Q49WN01 TO Q49WN15/101

COLUMN A EPA Number AND description of waste shipped off site for use, reuse, recycling, or reclamation	COLUMN B EPA Identification Numbers of three facilities to which waste was sent in greatest volume for use, reuse recycling, or reclamation	COLUMN C Quantity of waste shipped to each facility during 1981*
a. Q49A01 Description: Q49A02 Q49A03	Q49BA101 Q49BA201 Q49BNC1 Q49BA103 Q49BA203 Q49BNC3 Q49BA102 Q49BA202 Q49BA03	Q49C01 Q49C02 Q49C03
b. Q49A04 Description: Q49A05 Q49A06	Q49BA104 Q49BA204 Q49BNC4 Q49BA105 Q49BA205 Q49BNC5 Q49BA106 Q49BA206 Q49BNC6	Q49C04 Q49C05 Q49C06
c. Q49A07 Description: Q49A08 Q49A09	Q49BA107 Q49BA207 Q49BNC7 Q49BA108 Q49BA208 Q49BNC8 Q49BA109 Q49BA209 Q49BNC9	Q49C07 Q49C08 Q49C09
d. Q49A10 Description: Q49A11 Q49A12	Q49BA110 Q49BA210 Q49BNC10 Q49BA111 Q49BA211 Q49BNC11 Q49BA112 Q49BA212 Q49BNC12	Q49C10 Q49C11 Q49C12
e. Q49A13 Description: Q49A14 Q49A15	Q49BA113 Q49BA213 Q49BNC13 Q49BA114 Q49BA214 Q49BNC14 Q49BA115 Q49BA215 Q49BNC15	Q49C13 Q49C14 Q49C15

*[CIRCLE ONE]:

Metric tonnes. 01

English (or short) tons. 02

Gallons. 03

Other [SPECIFY]: Q49C4C01 to Q49C4C15 04

COLUMN A: ENTER THE EPA WASTE NUMBERS AND SHORT DESCRIPTIONS OF THE FIVE WASTES, INCLUDING DESCRIPTIONS OF THE PROCESSES THROUGH WHICH EACH WASTE WAS GENERATED. [EPA WASTE CODES ARE LISTED IN APPENDIX A OF THE GENERAL INSTRUCTIONS]

COLUMN B: ENTER THE EPA IDENTIFICATION NUMBERS OF THE THREE FACILITIES TO WHICH EACH WASTE WAS SHIPPED IN GREATEST VOLUME.

COLUMN C: INDICATE THE QUANTITY OF WASTE SHIPPED TO EACH FACILITY AND CIRCLE THE UNIT CODE AT THE BOTTOM OF THE COLUMN. PLEASE USE THE SAME UNIT OF MEASURE FOR ALL WASTES IN THE TABLE.

COLUMN D: CIRCLE THE CODE OR CODES THAT INDICATE HOW EACH WASTE WAS STORED PRIOR TO SHIPMENT OFF SITE FOR USE, REUSE, RECYCLING, OR RECLAMATION.

COLUMN E: FOR EACH FACILITY, INDICATE THE AVERAGE NUMBER OF DAYS EACH WASTE WAS STORED PRIOR TO SHIPMENT OFF SITE FOR USE, REUSE, RECYCLING, OR RECLAMATION. 19R

COLUMN D: How was waste stored prior to shipment off site for use, reuse, recycling, or reclamation? [CIRCLE ALL THAT APPLY FOR EACH FACILITY]						COLUMN E: Average number of days waste was stored prior to shipment off site for use, reuse, recycling, or reclamation.
In containers	In above ground tanks	In below ground tanks	In piles	In surface impoundments	Other [SPECIFY]:	
Q49C01 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D601	Q49E01 Days
Q49C02 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D602	Q49E02 Days
Q49C03 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D603	Q49E03 Days
Q49C04 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D604	Q49E04 Days
Q49C05 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D605	Q49E05 Days
Q49C06 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D606	Q49E06 Days
Q49C07 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D607	Q49E07 Days
Q49C08 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D608	Q49E08 Days
Q49C09 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D609	Q49E09 Days
Q49C10 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D610	Q49E10 Days
Q49C11 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D611	Q49E11 Days
Q49C12 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D612	Q49E12 Days
Q49C13 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D613	Q49E13 Days
Q49C14 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D614	Q49E14 Days
Q49C15 01	Q49C02 02	Q49C03 03	Q49C04 04	Q49C05 05	06 Q49D615	Q49E15 Days

(coding batch 7) Q49C801 to Q49C815

50. Please complete the following table for the five principal hazardous wastes which this facility used, reused, recycled, or reclaimed, on site in greatest volume during the 1981 calendar year. [REFER TO FACING PAGE FOR INSTRUCTIONS FOR COMPLETING EACH COLUMN OF THE TABLE]

IF THIS FACILITY DID NOT USE, REUSE, RECYCLE, OR RECLAIM ANY HAZARDOUS WASTES ON SITE IN 1981, CHECK HERE ☐ AND SKIP TO QUESTION 52. Q30x50 /102

/103

COLUMN A	COLUMN B — How was this waste used, reused, recycled or reclaimed? [CIRCLE ALL THAT APPLY]					COLUMN C
EPA Number AND description of waste used, reused, recycled or reclaimed on site	As feedstock in manufacturing process	As fuel or fuel supplement	In manner constituting disposal	Reclaimed	Other [SPECIFY]:	Quantity of waste used, reused, recycled or reclaimed during 1981*
a. |__|__|__|__| Description: Q50A01	01 Q50B01	02 Q50B201	03 Q50B301	04 Q50B401	05 Q50B501	Q50C01
b. |__|__|__|__| Description: Q50A02	01 Q50B102	02 Q50B202	03 Q50B302	04 Q50B402	05 Q50B502	Q50C02
c. |__|__|__|__| Description: Q50A03	01 Q50B103	02 Q50B203	03 Q50B303	04 Q50B403	05 Q50B503	Q50C03
d. |__|__|__|__| Description: Q50A04	01 Q50B104	02 Q50B204	03 Q50B304	04 Q50B404	05 Q50B504	Q50C04
e. |__|__|__|__| Description: Q50A05	01 Q50B105	02 Q50B205	03 Q50B305	04 Q50B405	05 Q50B505	Q50C05

*[CIRCLE ONE]:

Metric tonnes 01
English (or short) tons 02
Gallons 03
Other [SPECIFY]: Q50C401 → Q50C405 04

COLUMN A: ENTER THE EPA WASTE NUMBERS AND SHORT DESCRIPTIONS OF THE FIVE WASTES, INCLUDING THE NAMES OF THE WASTES AND DESCRIPTIONS OF THE PROCESSES THROUGH WHICH EACH WASTE WAS GENERATED. [EPA WASTE CODES ARE LISTED IN APPENDIX A OF THE GENERAL INSTRUCTIONS]

COLUMN B: CIRCLE THE CODE OR CODES THAT DESCRIBE HOW THIS WASTE WAS USED, REUSED, RECYCLED OR RECLAIMED DURING 1981.

COLUMN C: INDICATE THE AVERAGE QUANTITY OF WASTE USED, REUSED, RECYCLED OR RECLAIMED DURING 1981 AND CIRCLE THE UNIT CODE AT THE BOTTOM OF THE TABLE. PLEASE USE THE SAME UNIT OF MEASURE FOR ALL WASTES IN THE TABLE.

COLUMN D: CIRCLE THE CODE OR CODES THAT INDICATE HOW EACH WASTE WAS STORED PRIOR TO USE, REUSE, RECYCLING, OR RECLAMATION.

COLUMN E: FOR EACH FACILITY, INDICATE THE AVERAGE NUMBER OF DAYS EACH WASTE WAS STORED PRIOR TO USE, REUSE, RECYCLING, OR RECLAMATION.

COLUMN D: How was waste stored prior to use, reuse, recycling, or reclamation? [CIRCLE ALL THAT APPLY]						COLUMN E: Average number of days waste was stored prior to use, reuse, recycling, or reclamation:
In containers	In above ground tanks	In below ground tanks	In piles	In surface impoundments	Other [SPECIFY]:	
01	02	03	04	05	06 _____	_____ Days
Q5D101	Q5D201	Q5D301	Q5D401	Q5D501	Q5D601	Q5E01
01	02	03	04	05	06 _____	_____ Days
Q5D102	Q5D202	Q5D302	Q5D402	Q5D502	Q5D602	Q5E02
01	02	03	04	05	06 _____	_____ Days
Q5D103	Q5D203	Q5D303	Q5D403	Q5D503	Q5D603	Q5E03
01	02	03	04	05	06 _____	_____ Days
Q5D104	Q5D204	Q5D304	Q5D404	Q5D504	Q5D604	Q5E04
01	02	03	04	05	06 _____	_____ Days
Q5D105	Q5D205	Q5D305	Q5D405	Q5D505	Q5D605	Q5E05

(coding batch #) Q5CB01 TO Q5CB05

51. For each waste indicated in Question 50 as being used in a manner constituting disposal ("03" circled in Column B), please describe the specific manner in which the waste was used.

Q 5

/16-17

X. FINANCIAL ASSURANCE

52. How will closure and/or post closure costs be covered for this facility? [CIRCLE ONE CODE FOR EACH COVERAGE METHOD]

COVERAGE BY:	Closure costs only	Post-closure costs only	Both closure and post-closure	Neither closure nor post-closure	
a. Trust fund. . . . . Q52A. . .	1	2	3	4	/18
b. Surety bond . . . . . Q52B. . .	1	2	3	4	/19
c. Letter of credit. . . . Q52C. .	1	2	3	4	/20
d. Financial test. . . . . Q52D. .	1	2	3	4	/21
e. Insurance policy. . . . Q52E. .	1	2	3	4	/22
f. Corporate guarantee . . . Q52F. .	1	2	3	4	/23
g. State guarantee . . . . . Q52G. .	1	2	3	4	/24
h. Federal or state exemption. Q52H. .	1	2	3	4	/25
i. Other [SPECIFY]: Q52I1	1	2	3	4	/26
Q52I2					/27

53. What are the annual administrative charges for maintaining the financial assurance mechanisms listed in Question 52?

	Dollars per year	
a. Closure.	$ Q53A	/29-37
b. Post-closure	$ Q53B	/38-46
c. TOTAL ADMINISTRATIVE COSTS. . .	$ Q53C	/47-55

54. Did this facility or the company that owns this facility put up collateral for financial assurance coverage? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 55] . . . . . Q.54 . . . 1 /56
No [SKIP TO QUESTION 56]. 2

55. What is the value of the collateral?

VALUE OF COLLATERAL: $ _____ Q.55 /57-65

56. Does this facility have liability insurance for third party damages (i.e., bodily injury and property damage) resulting from sudden or nonsudden releases of hazardous waste? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 57] . . . . . Q.56 . 1
No [PLEASE SIGN THE CERTIFICATION STATEMENT ON PAGE 37 AND RETURN THIS FORM TO EPA]. . . . . 2 /66

57. In what year did this facility obtain liability insurance for third party damages? [IF MORE THAN ONE POLICY HAS BEEN WRITTEN FOR THIS FACILITY, PLEASE GIVE THE YEAR THE MOST RECENT POLICY WAS OBTAINED]

YEAR LIABILITY INSURANCE OBTAINED: _____ Q.57 67-71

58. In order to obtain liability insurance, was it necessary to upgrade this facility, modify current practices at this facility, or have a risk assessment of this facility performed? [CIRCLE ONE CODE FOR EACH ITEM]

	Yes	No	
a. Upgrade facility. Q.58A	1	2	/76
b. Modify current practices. Q.58B	1	2	/77
c. Obtain risk assessment. Q.58C	1	2	/78

59. How many facilities, INCLUDING this facility, does the liability insurance cover?

NUMBER OF FACILITIES COVERED: _____ Q.59 79-81

60. In the table below, please indicate the number of policies held, the amount of coverage, the annual cost of the policy, and the amount of the deductible for the liability insurance. [IF MORE THAN ONE POLICY IS HELD, INDICATE THE TOTAL COVERAGE, THE TOTAL COST, AND THE AVERAGE DEDUCTIBLE FOR ALL POLICIES IN EACH CATEGORY OF THE TABLE BELOW]

IF MORE THAN ONE FACILITY IS COVERED BY THE POLICY, CHECK HERE ☐ AND ENTER THE AMOUNT OF COVERAGE, COST AND DEDUCTIBLE FOR ALL FACILITIES COVERED. Q60X60 /82

/221

Type of Policy	Number of Policies	Amount of Coverage	Annual Cost of Policy	Amount of of Deductible
a. Sudden	Q60A1	Q60A2	Q60A3	Q60A4
b. Nonsudden	Q60B1	Q60B2	Q60B3	Q60B4
c. Combined policy	Q60C1	Q60C2	Q60C3	Q60C4

/16-44

/45-97

/74-102

61. Does the policy cover accidents resulting from sudden or nonsudden releases of hazardous waste which may have occurred prior to the year in which the policy was obtained? [CIRCLE ONLY ONE CODE]

Yes [GO ON TO QUESTION 62]. . . . . Q.61. . 1 /103

No [SKIP TO QUESTION 63] 2

62. For how many years prior to the year the policy was obtained is accident liability insurance provided?

NUMBER OF YEARS PRIOR COVERAGE: Q62 /104-105

63. Does the policy cover legal defense costs? [CIRCLE ONLY ONE CODE]

Yes. . . . . Q.63. . 1 /106

No 2

PLEASE SIGN THE CERTIFICATION STATEMENT ON PAGE 37 AND RETURN THIS FORM TO EPA IN THE ENVELOPE PROVIDED.

CERTIFICATION STATEMENT

THE OWNER OR THE OPERATOR OF THE FACILITY, OR HIS AUTHORIZED REPRESENTATIVE, MUST SIGN AND DATE THE CERTIFICATION WHERE INDICATED. THE PRINTED OR TYPED NAME OF THE PERSON SIGNING THE CERTIFICATION MUST ALSO BE INCLUDED WHERE INDICATED.

CERTIFICATION:

I certify under penalty of law that I have personally examined and am familiar with the information submitted in this and all attached documents, and that based on my inquiry of those individuals immediately responsible for obtaining the information, I believe that the submitted information is true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment.

PRINT OR TYPE NAME	SIGNATURE	DATE SIGNED

AFTER COMPLETING THIS QUESTIONNAIRE, RETURN IT TO EPA IN THE ENVELOPE ENCLOSED IN THE QUESTIONNAIRE PACKAGE.

IF THIS FACILITY HAS RECEIVED MORE THAN ONE QUESTIONNAIRE, PLEASE RETURN ALL COMPLETED QUESTIONNAIRES IN THE SAME ENVELOPE.

OMB No: 2000-0396
Expiration Date: 6/30/84

RCRA Section 3007 Questionnaire

Organic Rubber Processing Chemicals Manufacturing Industry

Return within 45 days from date of receipt to:

Ms. Dina Villari (WH 562)
Characterization and Assessment Division
Office of Solid Waste
U.S. Environmental Protection Agency
401 M St., S.W.
Washington D.C. 20460

1. Corporate/Plant Data

A. Name of Corporation _____

B. Address of Corporation Headquarters

Street _____

City _____ State _____ Zip _____

C. Name of Plant _____

D. Address of Plant

Street _____

City _____ State _____ Zip _____

Hazardous waste generator ID number: _____

E. Mailing Address of Plant (if different from above)

_____

F. Name(s) of personnel to be contacted for additional information pertaining to this questionnaire

Name	**Title**	**Telephone**
_____	_____	_____
_____	_____	_____
_____	_____	_____

2. Type of Plant Operation

A. Indicate whether the following organic rubber processing chemicals[1] were manufactured at this facility in 1983:[2]

1. CAS No.:
   Chemical Name:
   Manufactured: ☐ Yes ☐ No
2. CAS No.:
   Chemical Name:
   Manufactured: ☐ Yes ☐ No
3. CAS No.:
   Chemical Name:
   Manufactured: ☐ Yes ☐ No
4. CAS No.:
   Chemical Name:
   Manufactured: ☐ Yes ☐ No
5. CAS No.:
   Chemical Name:
   Manufactured: ☐ Yes ☐ No
6. CAS No.:
   Chemical Name:
   Manufactured: ☐ Yes ☐ No
7. CAS No.:
   Chemical Name:
   Manufactured: ☐ Yes ☐ No
8. CAS No.:
   Chemical Name:
   Manufactured: ☐ Yes ☐ No
9. CAS No.:
   Chemical Name:
   Manufactured: ☐ Yes ☐ No
10. CAS No.:
    Chemical Name:
    Manufactured: ☐ Yes ☐ No

Complete this questionnaire for each chemical listed above which you manufactured. If none of these chemicals were manufactured, return pages 1 and 2 of this questionnaire.

B. Identify as follows the chemical intermediate(s)[3] produced at this facility in the production of the chemicals identified above:

CAS Number	Chemical Name	Common Name

[1] Rubber processing chemicals are defined as the synthetic organic compounds that are added to natural or synthetic rubber to produce or enhance specific properties in the final product.

[2] If additional space is needed for listing products or intermediates, attach an additional sheet.

[3] Intermediate means any chemical substance (1) which is intentionally manufactured and removed from the equipment in which it is manufactured, and (2) which either is consumed in whole or in part in chemical reactions(s) used for the intentional manufacture of other chemical substance(s) or mixture(s).

C. Indicate those classes of chemical products or intermediates which were produced at this facility in 1983. Circle appropriate code number(s).

Code Number	Classes of Products and Intermediates	Code Number	Classes of Products and Intermediates	Code Number	Classes of Products and Intermediates
ORGANIC DYES & PIGMENTS		286 67	Halogenated Aromatics NEC	286 84	Acyclic Acids, Anhydrides & Esters
286 52	Organic Dyes	286 68	Alicyclic Chemicals	286 85	Acyclic Aldehydes
286 53	Organic Pigments	286 69	Cyclic Intermediates NEC	286 86	Acyclic Ketones
CYCLIC INTERMEDIATES		CYCLIC CHEMICALS NEC		286 87	Acyclic Nitrogens
286 61	Aromatic Acids & Derivatives	286 71	Salts of Aromatic Acids	286 88	Acyclic Compounds NEC
286 62	Aromatic Acids, Anhydrides & Esters	286 72	Other Cyclic Chemicals	286 89	Acyclics NEC
286 63	Aromatic Ketones & Aldehydes	ACYCLIC CHEMICALS		ORGANIC CHEMICALS NEC	
286 64	Aromatic Alcohols	286 81	Halogenated Hydrocarbons	286 91	Flavor & Perfume Materials
286 65	Aromatic Hydrocarbons	286 82	Monohydric Acyclic Alcohols	286 93	Plasticizers
286 66	Cyclic Amines	286 83	Polyhydric Alcohols & Ethers	NEC – Not elsewhere classified	

3. Process and Treatment Residual Information

This information will be used to address industry wide variation in type and quantity of residuals generated. Residuals include any process stream generated during the manufacture of a product which is not used as a raw material or principally sold as a commercial product. Treatment residuals include wastes from the treatment of process residuals. Residuals may be solids (e.g., still bottoms), liquids (e.g., wastewater), confined gases (e.g., gases that are containerized to facilitate disposal), and unconfined gases generated by the management of solid or liquid residuals (e.g., incinerator stack emissions) or unconfined gases containing condensable gases (e.g., vented light ends).

For each unit process provide a general process block flow diagram that identifies major unit operations and treatment processes and indicates the types and points of introduction/generation of feedstocks, products, co-products/by-products, and residuals (See Examples I and II.) Include the information requested in Questions 3-A through 3-D in the flow diagram. Provide the information requested in Questions 3-E and 3-F in an attachment.

A. Identify the product process, intermediates, co-products and by-products produced by the process.

B. Provide a block for each major unit operation (e.g., reactor, washer, filtration, air emission control, aeration lagoon, etc.) in the production process and in each residuals management process.

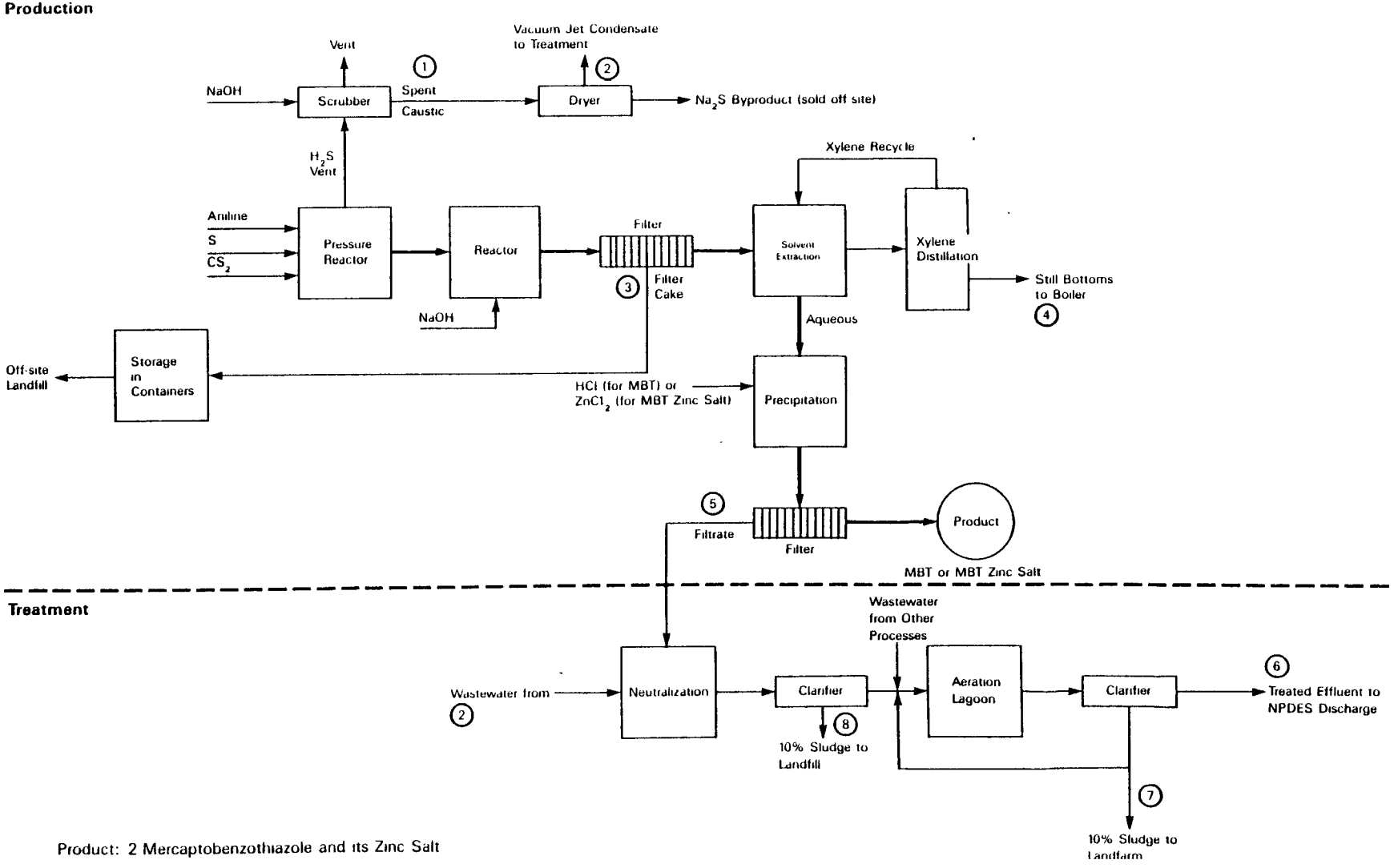
C. Identify process input such as raw materials, reagents and solvents by chemical or common name or chemical formula, and indicate the point of introduction with arrows.

D. Assign a Residual Identification Number to each of the following types of residuals and indicate its point of generation with an arrow:

1. Residuals generated by unit operations in the product process, including unit operations that produce/recover co-products, by-products and solvents; and
2. Final treatment residuals (i.e., residuals generated by physical, chemical (including incineration and other thermal treatment) or biological treatment and that are not intermediate treatment residuals generated within a treatment train).

When more than one process block flow diagram is provided (i.e., for multiple product processes), assign unique, sequential Residual Identification Numbers to the residuals for each flow diagram.

Example I — Process Block Flow Diagram



Product: 2 Mercaptobenzothiazole and its Zinc Salt

Intermediates: None

E. If residuals from this product process are combined with the residuals from other product processes at this facility prior to treatment, identify the product process residual by Residual Identification Number and specify the source of the other residuals using the codes provided in Question 2-C.

F. Indicate the typical annual production, the 1983 production, and system capacity (specify), for each: product, co-product and by-product.

Example II — Response to Questions 3-E and 3-F

Product Process: 2-Mercaptobenzothiazole, Zinc salt (MBT) Production

A. Mixing of MBT Production Residuals with Other Residuals

MBT Residual Identification Number (from Flow Diagram)	Source of Other Residuals (Manufacturing Code from Question 2-B)
2,5	286 66, 286 65

B. Annual Production (1983)

Product	
Technical MBT	1,000,000 lbs (1983)
	1,500,000 lbs (typical)
	2,000,000 lbs (capacity)
MBT, Zinc Salt	12,500,000 lbs (1983, typical)
	15,000,000 lbs (capacity)
Co-product/By-product	
Sodium Sulfide	250,000 lbs (1983)
	300,000 lbs (typical)
	400,000 lbs (capacity)

4. Residuals Characterization Information

For each process used to manufacture the chemicals listed in Question 2, complete Table 1 by providing the following information for each identified residual. An example is provided below (Example III).

A. Identify the product process.

B. List each residual by Residual Identification Number (include by-products and residuals generated from the treatment of process residuals.)

C. If the residual has been identified in the facility RCRA notification, indicate whether it was identified as ignitable (I), corrosive (C), reactive (R), EP toxic (E), listed by EPA or reported by the facility as toxic (T), or acutely hazardous (H).

D. For each residual, describe the following properties where appropriate: physical state [e.g., liquid (specify whether aqueous or organic), solid, slurry (indicate solids content), gas]; pH; flash point; Btu content; viscosity; toxicity.

E. List the compounds which are known by analysis to be present in the residual and specify, as known, the concentration ranges as follows:

Code	Range
A	> 50%
B	> 10% to 50%
C	> 1% to 10%
D	> 0.1% to 1%
E	> 0.01% to 0.1%
[Actual concentration]*	≤ 0.01%

F. If residual analyses are not available, list the compounds which are expected to be present in the residual and expected concentrations based on chemical engineering principles.

Example III — Response to Question 4

A. Product Process: MBT Production

B. Residual Identification Number	C. RCRA Identification (I,C,R,E,T, or H)	D. Properties of Residual	E. Known Compounds, Concentrations, Ranges	F. Other Expected Compounds
3	Not identified	Solid	Sulfur: C	
			Aniline: C	Carbon Disulfide
			MBT: C	
			Sodium Sulfide: C	
6	Not identified	Aqueous Liquid	Water: A	
		pH = 7.8	MBT: 200 ppm	

Table I — Response to Question 4

A. Product Process: _____

B. Residual Identification Number	C. RCRA Identification (I,C,R,E,T, or H)	D. Properties of Residual	E. Known Compounds, Concentrations, Ranges	F. Other Expected Compounds

*RESIDUAL CONSTITUENT CONCENTRATION CODE

Code	Range
A	> 50%
B	> 10% to 50%
C	> 1% to 10%
D	> 0.1% to 1%
E	> 0.01% to 0.1%
[Actual concentration]†	≤ 0.01%

† If concentration is less than 0.01%, specify, as known, the typical concentration in ppm

5. Residuals Management Information — General

For each process used to manufacture the chemicals listed in Question 2, complete Table II by providing the following information for each identified residual. An example is provided below. (Example IV).

A. Identify the product process.

B. Specify the Residual Identification Number.

C. Specify residual category in accordance with codes provided.

Code	Categories of Residuals
C1.	Process precipitates or filtration residues and process sludges
C2.	Process decantates or filtrates
C3.	Treatment sludges: (specify) a. biological b. other
C4.	Spent activated carbon or other adsorbent (specify)
C5.	Spent catalyst
C6.	Heavy ends: a. distillation residues b. misc. heavy ends
C7.	Spent solvents
C8.	Untreated process wastewater: a. acid b. caustic c. neutral[1]
C9.	Treated wastewater discharge
C10.	Containers, liners, cleaning rags, gloves, etc.
C11.	Off specification products and feedstock
C12.	Other (specify)
C13.	By-product
C14.	Light ends: a. condensable[2] b. noncondensable

[1]Acidic: pH < 2.0, Neutral $2.0 \leq$ pH ≤ 12.0, Caustic, pH > 12.0

[2]Light ends are condensable if primarily composed of gases which are liquid at ambient temperature and pressure.

D. Specify management methods in accordance with codes provided. If a residual is subject to a sequence of methods (e.g., storage in a tank, incineration), list the methods in sequence. If a residual is handled alternatively by more than one method (e.g., either incinerated or burned in a boiler), identify the alternate methods.

Code	Management Methods
M1.	Storage in: a. tank b. container c. pile d. surface impoundment
M2.	Treatment in: a. tank b. container c. surface impoundment
M3.	Burning in boiler
M4.	Recovery/reclamation: a. recovery b. reused same process c. reused different process d. sales
M5.	Incineration
M6.	Landfill
M7.	Underground injection
M8.	On-site wastewater treatment in: a. tank b. surface impoundment c. container
M9.	Discharge to publicly owned wastewater treatment works
M10.	Discharge to surface water under NPDES
M11.	Discharge to off-site privately owned wastewater treatment works
M12.	Other (specify)
M13.	Scrubber: a. caustic b. water c. other (specify)
M14.	Flare

E. Indicate the amount of each residual managed by each method in 1983 (specify units). Include any clarification needed to describe the waste stream.

F. Indicate whether the residual is managed on-site or off-site. If managed off-site, identify the site in the space provided in Table III.

G. For residuals managed off-site, except for discharges to a POTW or surface water under a NPDES permit, indicate the average management cost per unit quantity of residual in 1983.

H. Indicate planned changes in residual management methods by specifying the codes for the new management methods, and indicate the anticipated date of change.

Example IV — Responses to Question 5

A. Product Process: MBT Production

B. Residual Identification Number	C. Residual Code	D. Management Code	E. 1983 Residual Quantities	F. On-site or Off-site Management	G. Costs for Off-site Management	H. Changes in Management Methods
1	C8	M4-a	25,000,000 gal*	On-site	N.A.	None
		(Sodium sulfide		recovery		None
		recovery)				
3	C1	M1-c	400 tons	On-site storage	NA	None
		M-6		Off-site disposal	$15/wet ton	M4 (1984)
6	C9	M-10	50 million gal.	Off-site	N.A.	None

*Prior to drying stage, Na_2S content is approximately 5% by weight of Residual #1.

Table II — Response to Question 5

A. Product Process: _____

B. Residual Identification Number	C. Residual Code	D. Management Code	E. 1983 Residual Quantities (specify units)	F. On-site or Off-site Management*	G. 1983 Costs for Off-site Management (cost/ton)	H. Changes in Management Methods

*Identify off-site waste management or recycling/reuse facility as indicated in the following Table (Table III).

Table III — Response to Question 5-F

Name of Facility: _____

Residual Identification Numbers: _____

Facility Mailing Address:

Street or P.O. Box: _____

City or Town: _____

State: _____ Zip: _____

Facility Location (if different from above):
Street, Route Number or Other Specific Identifier:

_____

City or Town: _____

State: _____ Zip: _____

Hazardous Waste Facility I.D. Number (if any):

_____

Name of Facility: _____

Residual Identification Numbers: _____

Facility Mailing Address:

Street or P.O. Box: _____

City or Town: _____

State: _____ Zip: _____

Facility Location (if different from above):
Street, Route Number or Other Specific Identifier:

_____

City or Town: _____

State: _____ Zip: _____

Hazardous waste Facility I.D. Number (if any):

_____

6. Specific On-site Residuals Management Information

Provide specific information for residuals managed on-site using available information to complete the following sections which pertain to your residuals management operations.

A. Storage or Treatment in Tanks*
B. Storage or Treatment in Containers*
C. Storage or Treatment in Piles*
D. Burning in a Boiler
E. Incineration
F. Land Treatment*
G. Surface Impoundments*
H. Landfills*

*If residuals are managed by these methods, provide the following information:

(1) Are groundwater monitoring data available? ☐ Yes ☐ No

(2) Are geologic or hydrogeologic data available? ☐ Yes ☐ No

A. Storage or Treatment in Tanks

Have identified residuals been stored or treated in on-site tanks at any time since January 1, 1983? ☐ Yes ☐ No

If yes, provide the following information for the 10 largest tanks:

Tank	Residuals Managed[1]	Design Capacity[2]	Storage or Treatment	Type of Treatment Used[3]	Avg. Length of Storage	Part of Wastewater Treatment Train[4] (Circle Yes or No)	Covered (Circle Yes or No)	Secondary Containment Provided[5] (Circle Yes or No)
1						Yes No	Yes No	Yes No
2						Yes No	Yes No	Yes No
3						Yes No	Yes No	Yes No
4						Yes No	Yes No	Yes No
5						Yes No	Yes No	Yes No
6						Yes No	Yes No	Yes No
7						Yes No	Yes No	Yes No
8						Yes No	Yes No	Yes No
9						Yes No	Yes No	Yes No
10						Yes No	Yes No	Yes No

[1]Use Residual Identification Numbers to identify residuals.

[2]Use the following codes to designate the tank capacity:

A ≤10,000 gallons
B >10,000 gallons to 100,000 gallons
C >100,000 gallons to 1,000,000 gallons
D >1,000,000 gallons

[4]Treatment train from which wastewater is discharged under a NPDES permit or through a sewer system to a publicly-owned treatment works.

[5]Secondary containment is provided when the tank is located inside a dike area where the volume of liquid that the diked area can contain is at least equivalent to the capacity of the largest tank.

B. Storage or Treatment in Containers*
Have identified residuals been stored or treated on-site in containers at any time since January 1, 1983? ☐ Yes ☐ No

If yes, provide the following information (if the facility has several container storage areas, provide information only on the primary container storage area):

1. Check typical and maximum quantity stored on any day in 1983 for each residual:

Residual No.[1]	Average Daily Quantity[2]	Maximum Daily Quantity[2]	Average Length of Storage

[1]Use Residual Identification Number to identify residuals
[2]Use the following code to designate the quantity of residual(s) in storage on any day in 1983:
A ≤ 550 gallons
B > 550 to 5500 gallons
C > 5500 to 55,000 gallons
D > 55,000 gallons

2. Identify the storage area base material:

☐ Concrete ☐ Asphalt ☐ Soil ☐ Other (specify) _____

3. If liquid residuals or residuals containing free liquids† are stored, is the storage area designed and operated to collect and contain surface runoff?

☐ Yes ☐ No ☐ Liquids are not stored

*Container means any portable device in which residuals were stored, treated or otherwise handled.
†A residual contains free liquids if liquids readily separate from the solid portion of the residual under ambient temperature and pressure.

C. Storage or Treatment in Piles

Have identified residuals been stored or treated in on-site piles at any time since January 1, 1983? ☐ Yes ☐ No

If yes, provide the following information for the 10 largest piles:

Pile	Residuals Managed[1]	Typical Quantity[2] Managed	Under Roofed Structure (Circle Yes or No)		Containment[3] Provided (Circle Yes or No)		Synthetic[4] Liner Base (Circle Yes or No)	
1	_____	_____	Yes	No	Yes	No	Yes	No
2	_____	_____	Yes	No	Yes	No	Yes	No
3	_____	_____	Yes	No	Yes	No	Yes	No
4	_____	_____	Yes	No	Yes	No	Yes	No
5	_____	_____	Yes	No	Yes	No	Yes	No
6	_____	_____	Yes	No	Yes	No	Yes	No
7	_____	_____	Yes	No	Yes	No	Yes	No
8	_____	_____	Yes	No	Yes	No	Yes	No
9	_____	_____	Yes	No	Yes	No	Yes	No
10	_____	_____	Yes	No	Yes	No	Yes	No

[1]Use Residual Identification Numbers to identify residuals.

[2]Use the following code to designate the typical quantity of residual(s) contained in the pile on any day in 1983:

- A ≤20 cubic yards
- B >20 to 200 cubic yards
- C >200 to 2,000 cubic yards
- D >2,000 to 20,000 cubic yards
- E >20,000 cubic yards

[3]Containment is provided when the pile base is designed, operated, and maintained to contain leachate and run-off.

[4]Is a synthetic liner installed in the pile base? Waste may lie directly on synthetic liner or the liner may be covered with clay layer.

D. Burning in a Boiler

Have identified residuals been burned in an on-site boiler at any time since January 1 1983? ☐ Yes ☐ No

If yes, provide the following information for each boiler:

1. Boiler and fuel type:

Type	Boiler Capacity (Heat Input in Million Btu/hr)	Primary Boiler Fuel	Percentage of Fuel Replaced by Residuals (Heat Input Basis)	Typical Boiler Load When Firing Residual (% of Capacity)	Boiler Temperature (°C) Inlet	Outlet
☐ Fire tube	☐ ≤10 million	☐ Oil	☐ ≤5%	☐ ≤50%	___	___
☐ Water tube	☐ >10 million to 100 million	☐ Gas	☐ >5-10%	☐ >50-75%		
		☐ Coal	☐ >10-25%	☐ >75%		
	☐ >100 million	☐ Wood or other	☐ >25-50%			
			☐ >50%			

2. Provide the following information for each of the residuals burned:

Residual No.[1]	Feed Rate (lbs. per hour)	Typical BTU Content (BTU/lb)	Typical Total Ash Content (% by wt.)	Typical Total Halogen Content (% by wt.)	Total Water Content (% by wt.)
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____

[1]Use Residual Identification Numbers to identify residuals.

3. Provide the following information on the total feed mixture when residual is burned:

Feed Rate (Pounds per hour) _____

Typical BTU Content (BTU/lb) _____

Typical Total Ash Content (% by wt.) _____

Typical Total Halogen Content (% by wt.) _____

Typical Total Water Content (% by wt.) _____

4. If the boiler is equipped with an air pollution control device, specify the type of device:

☐ Scrubber ☐ Electrostatic precipitator ☐ Other (specify) _____

5. Are residual-burning stack emissions data available? ☐ Yes ☐ No

E. Incineration

Have identified residuals been incinerated on-site at any time since January 1, 1983? ☐ Yes ☐ No

If yes, provide the following information for each incinerator:

1. Incinerator type:

Type	Incinerator Capacity (Heat Input in MMBtu/hr.)	Feed Type	Percentage of Auxiliary Fuel Required (Heat Input Basis)
☐ Liquid injection ☐ Rotary kiln ☐ Hearth ☐ Other_____ (specify)	☐ ≤10 million ☐ >10 million to 100 million ☐ >100 million	☐ Liquid – nozzle type _____(specify) – Atomizing pressure _____(specify) ☐ Solid ☐ Batch charge ☐ Continuous charge	_____

2. Combustion Chamber Design Parameters:

	Primary Chamber	Secondary Chamber
Combustion Chamber Temp.	_____ °C	_____ °C
Location of Temp. Monitor	_____	_____
Residence Time	_____ (sec)	_____ (sec)

3. If the incinerator is equipped with an air pollution control device, specify the type(s) of device(s):

☐ Scrubber ☐ Electrostatic precipitator ☐ Other (specify) _____

4. Are incinerator stack emissions data available? ☐ Yes ☐ No

5. Provide the following information for each of the residuals burned:

Residual No.[1]	Feed Rate (lbs. per hour)	Typical BTU Content (BTU/lb)	Typical Total Ash Content (% by wt.)	Typical Total Halogen Content (% by wt.)	Total Water Content (% by wt.)
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____
_____	_____	_____	_____	_____	_____

[1]Use Residual Identification Numbers to identify residuals.

F. Land Treatment

Have identified residuals been managed in an on-site land treatment operation at any time since January 1, 1983? ☐ Yes ☐ No

If yes, provide the following information:

1. Year land treatment initiated at site: _____

2. Year land treatment of identified residuals initiated: _____

3. Have residuals other than identified residuals been land treated at any time since January 1, 1983? ☐ Yes ☐ No

4. What was the total area actively used for land treatment in 1983? _____ acres

5. What is the average slope of the land treatment site? _____ percent

6. Is surface water run-off from the site collected for treatment, re-application to the site, or analyzed prior to discharge? ☐ Yes ☐ No

7. Check method(s) used to apply residuals to the land treatment site.

   a. ☐ Surface spreading or spray irrigation without plow or disc incorporation. Indicate residuals applied in this manner using Residual Identification Numbers: _____

   b. ☐ Surface spreading or spray irrigation with plow or disc incorporation to a depth of _____ (specify). Indicate residuals applied in this manner using Residual Identification Numbers: _____

   c. ☐ Subsurface injection to a depth of _____ (specify). Indicate residuals applied in this manner using Residual Identification Numbers: _____

   d. ☐ Other methods (specify methods and residuals): _____

8. Is soil core monitoring performed? ☐ Yes ☐ No

9. Is soil pore water monitoring performed? ☐ Yes ☐ No

G. Surface Impoundments*

Have identified residuals been stored, treated, or disposed of in an on-site surface impoundment at any time since January 1, 1983? ☐ Yes ☐ No

If yes, complete Table IV.

*A surface impoundent is defined as holding, storage, settling, and aeration pits, ponds, or lagoons formed primarily of earthen materials.

Table IV — Response to Question 6-G

If more than 5 surface impoundments have been used since January 1, 1983 to manage identified residuals, provide information only on the 5 impoundments with the largest capacities. Use Residual Identification Numbers to identify residuals. If you do not know whether a liner has been installed, circle both "Yes" and "No." If you do not know the thickness of a liner, indicate "UNK" for unknown.

					Synthetic Liner			Clay Liner			Leachate Collection System	
Impoundment	Residuals Disposed (RIN)	Total Capacity (Gallons)[1]	Storage or Treatment (specify)	Specify Treatment Type if Applicable[2]	Installed	Thickness (mils)	No. of Liners	Installed	Thickness (in)	No. of Liners	Installed	Leachate Generated
1					Yes No			Yes No			Yes No	Yes No
2					Yes No			Yes No			Yes No	Yes No
3					Yes No			Yes No			Yes No	Yes No
4					Yes No			Yes No			Yes No	Yes No
5					Yes No			Yes No			Yes No	Yes No

[1]Use the following code to designate the quantity of residual(s) in storage on any day in 1983:

A ≤ 550 gallons
B > 550 to 5,500 gallons
C > 5,500 to 55,000 gallons
D > 55,000 gallons

[2]Use the following codes to specify treatment type:

A Neutralization
B Settling/Clarification
C Aeration
D Equalization
E Mixing
F Evaporation
G Other (specify)

H. Landfills

1. Have identified residuals been landfilled on-site at any time that you owned or operated this facility? ☐ Yes ☐ No
   If yes, answer questions 2 and 3.

2. Has any on-site landfill (or landfill cell) that was used to dispose of identified residuals been closed (i.e, no longer used to dispose of wastes)? ☐ Yes ☐ No
   If yes, complete Table V.

3. Have any identified residuals been landfilled on-site at any time since January 1, 1983 in a cell that has not been closed? ☐ Yes ☐ No
   If yes, complete Table VI.

Table V — Response to Question 6-H-2

Closed Landfill Cells

If more than 5 cells containing identified residuals have been closed, provide information only on the 5 cells that were most recently closed. Use Residual Identification Numbers to identify residuals. If you do not know whether a layer or liner was installed, circle both "Yes" and "No." If you do not know the thickness of a layer or liner, indicate "UNK" for unknown.

A. Cap/Cover Design

Cell	Residuals Disposed (RIN)	Drainage Layer				Cap Design Clay Layer			Synthetic Liner			
		Installed		Material	Thickness (in)	Installed		Thickness (in)	Installed		Material	Thickness (Mils)
1	_____	Yes	No	_____	_____	Yes	No	_____	Yes	No	_____	_____
2	_____	Yes	No	_____	_____	Yes	No	_____	Yes	No	_____	_____
3	_____	Yes	No	_____	_____	Yes	No	_____	Yes	No	_____	_____
4	_____	Yes	No	_____	_____	Yes	No	_____	Yes	No	_____	_____
5	_____	Yes	No	_____	_____	Yes	No	_____	Yes	No	_____	_____

B. Bottom Liner Design/Leachate Collection

Cell Number (As Assigned Above)	Synthetic Liner				Clay Liner				Leachate Collection System			
	Installed		Thickness (mils)	No. of Liners	Installed		Thickness (in)	No. of Liners	Installed		Leachate Generated	
1	Yes	No	_____	_____	Yes	No	_____	_____	Yes	No	Yes	No
2	Yes	No	_____	_____	Yes	No	_____	_____	Yes	No	Yes	No
3	Yes	No	_____	_____	Yes	No	_____	_____	Yes	No	Yes	No
4	Yes	No	_____	_____	Yes	No	_____	_____	Yes	No	Yes	No
5	Yes	No	_____	_____	Yes	No	_____	_____	Yes	No	Yes	No

Table VI — Response to Question 6-H-3

Landfill Cells Used to Dispose of Identified Residuals at any Time Since January 1, 1983

If more than 5 cells have been used since January 1, 1983 to dispose of identified residuals, provide information only on the 5 containing the greatest quantities of identified residuals. Use Residual Identification Numbers to identify residuals. If you do not know whether a liner has been installed, circle both "Yes" and "No." If you do not know the thickness of a liner, indicate "UNK" for unknown.

Bottom Liner Design/Leachate Collection

		Synthetic Liner					Clay Liner				Leachate Collection System			
Cell	Residuals Disposed (RIN)	Installed		Material	Thickness (mils)	No. of Liners	Installed		Thickness (in)	No. of Liners	Installed		Leachate Genrated	
1	_____	Yes	No	_____	_____	_____	Yes	No	_____	_____	Yes	No	Yes	No
2	_____	Yes	No	_____	_____	_____	Yes	No	_____	_____	Yes	No	Yes	No
3	_____	Yes	No	_____	_____	_____	Yes	No	_____	_____	Yes	No	Yes	No
4	_____	Yes	No	_____	_____	_____	Yes	No	_____	_____	Yes	No	Yes	No
5	_____	Yes	No	_____	_____	_____	Yes	No	_____	_____	Yes	No	Yes	No

APPENDIX B

PROCESS STUDIES

1.0 INTRODUCTION

This appendix contains 22 exploratory studies of various industrial processes and practices known to generate (or influence the generation of) hazardous wastes. The list of the analyzed processes and practices is given below:

Study No.	Description
1	Acrylonitrile Manufacture
2	Agricultural Chemicals Formulation
3	Electroplating
4	Epichlorohydrin Manufacture
5	Inorganic Pigments Manufacture
6	Metal Surface Treatment
7	Organic Dyes & Pigments Manufacture
8	Paint Manufacturing
9	Petroleum Refining
10	Phenolic Resins Manufacture
11	Printed Circuit Boards Manufacture
12	Printing Operations
13	Synthetic Fiber Manufacture
14	Synthetic Rubber Manufacture
15	1,1,1-Trichloroethane Manufacture
16	Trichloroethylene/Perchloroethylene Manufacture
17	Vinyl Chloride Monomer Manufacture
18	Wood Preserving
19	Good Operating Practices
20	Metal Parts Cleaning
21	Paint Application
22	Process Equipment Cleaning

The studies were performed in order to accomplish the following set of objectives:

- Identify and characterize source reduction technologies currently being used.

- o Identify and characterize new technological approaches which may reduce waste generation.
- o Provide an assessment of the current extent of waste reduction achieved due to implementation of the considered methodology.
- o Provide an assessment of the future extent of waste reduction due to further implementation of both current and new technologies.

Accomplishing these objectives was approached in the manner outlined below.

2.0 APPROACH AND METHODOLOGY

It is important to note that source control measures are highly process- or site-specific. The preparation of a truly accurate assessment of the extent to which wastes have been and can be minimized by industry nationwide would require an extensive site-by-site inspection, coupled with engineering and economic analyses of many processes and large numbers of facilities. The simplified approach used here relies on the concept of an "average" process. The "average" process is one which represents a synthetic approximation of major variations encountered from facility to facility. Process configurations were evolved mainly from descriptions available in the public domain and general literature. In most cases, the appropriate degree of resolution was judged to be at the level of a generic block flow diagram.

The approach used to accomplish the objectives listed in Section 1 consisted of the following steps:

(a) Definition of a manageable set of waste-producing processes and practices to be analyzed.

(b) Data collection and engineering analysis of each process and practice to produce a comprehensive list of source reduction techniques, including those that are currently practiced and those that may be practiced in the future.

(c) Review of the compiled source reduction techniques by industry and consultants. In this review process, each technique would ideally receive an independent rating as to its waste reduction effectiveness, extent of current use and future application

potential. Additional objectives of such review consist of broadening the compilation to include techniques not considered originally and to limit the necessarily conjectural nature of some results obtained from part (b) above.

(d) Derivation of estimates for current and future extents of waste reduction for each process, based on ratings obtained from (c), and

(e) Derivation of nationwide estimates for the current and future extents of waste reduction, based on the composite profiles for each industry category. The industry composites are obtained, in turn, from the averaged extent of waste reduction achieved and potential future reduction for the individual representative processes.

The sample set of 22 processes and practices was selected based on EPA guidance, production volumes, the RIA Mail Survey database and on the "F" and "K" waste stream RCRA listings.

Data collection involved inspection of the pre-compiled source reduction bibliographies, automated bibliographic searches, consultation with standard references (e.g. Kirk-Othmer's Encyclopedia of Chemical Technology), government studies (e.g. U.S. EPA Effluent Guidelines development documents), and consultations with experts and industry contacts. After the data were compiled, a standardized format for data categorization was developed for each process and practice. Section 9 of each individual process study was prepared following identification of source control methods through preliminary engineering analysis of the process and review of the compiled information.

Following their description, all of the identified source control techniques were assembled in a summary table and preliminary ratings were generated by project staff for each source reduction technique in the following categories: waste reduction effectiveness, extent of current use, and future application potential. Additionally, ratings were given to the quantity and quality of the available data. All ratings were based on the integer scale of zero (none), one (low), two (medium), three (high), four (all). Product substitution options were identified mainly through database review and are described in a separate section (Section 10) of each process study.

Following the preparation of a preliminary draft, each process study was submitted for an independent review by interested industrial firms involved in that particular process. In other cases, the reviewers were independent consultants or resident technical staff with experience in a particular process.

The reviewers were asked to comment on the technical substance of the report with special emphasis on the integer ratings given to each source control technique. Additionally, the reviewers were asked to provide information on the actual source reduction applications known to them and to augment the compiled list with any techniques that they felt were worth considering.

After the individual process study review comments were received and evaluated, drafts were revised and the extent of waste reduction due to source control was computed for each study from the ratings developed using the computational methodology described below. Waste reduction estimates were calculated for each wastestream and for each process overall.

For each process, two sets of numbers were generated:

1) Qualitative estimates of waste reductions which firms as a group are currently achieving, and

2) Qualitative estimates of waste reductions achievable in the future using techniques suggested and identified in the study.

The intent in furnishing these qualitative estimates is to provide a basis for crude projections of the overall extent of waste reduction possible for the entire industry. Under no circumstances should these estimates be construed as definitive thresholds or limits on reductions achievable by the individual firms employing the analyzed process.

It must be noted that, in many cases, both RCRA and non-RCRA wastestreams were analyzed for their minimization potential. This was done primarily because of concern that control of non-RCRA waste streams can be indirectly responsible for RCRA waste generation. For example, control of solvent

emissions into the air has, in the past, been frequently accomplished using adsorption on activated carbon. The regeneration of carbon using steam produced in certain cases a non-recyclable mixture of solvent and water that had to be disposed of.

The interactions between hazardous and non-hazardous wastes are complex and not readily visible. Therefore, it was deemed prudent to apply the analysis to all principal wastestreams or residuals and not just to those which are considered RCRA streams under current regulations. However, each process study clearly differentiates between the listed RCRA "F" and "K" wastes and other streams, and this distinction is utilized in the final analysis (see Section 3 of the main report).

3.0 COMPUTATIONAL PROCEDURES

The text below explains how qualitative ratings based on engineering judgement were given to effectiveness, extent of current use, and future application potential for each source control method and how they were combined to yield qualitative estimates of the waste that has been reduced based on current practice and the degree of reduction achievable based on potential future practices. These estimates, or indices, were determined for each individual method, each individual wastestream, and each individual process or study. Following the discussion of methodology development, sample calculations are provided.

Current Waste Reduction Index

The current waste reduction index (C) is a qualitative measure of past waste reduction from the employment of current waste reduction measures. In other words, it represents the reduction in waste that occurred because of measures already implemented. The derivation of equations allowing for computation of C from the ratings given to each waste reduction method is presented below.

Consider a process which, in the past, generated waste at a specific rate W_p. Assume that due to implementation of certain source control techniques, the same process now generates waste at a specific rate W_o. Hence, the current overall reduction index of waste generated is:

$$(1) \quad C = S\,(W_p - W_o)/W_p$$

where:
- C = current reduction index of waste produced by the process. Index is based on a range of 0 to S (for this study, a range of 0 to 4 was employed).
- S = the upper bound of the integer range selected (4).
- W_p = past specific waste generation rate (lbs waste/lbs product).
- W_o = current specific waste generation rate (lbs waste/lbs product).

Now consider that the process has N different wastestreams and that for each wastestream (j, where j=1,2,..N) there are M different source control methods (i, where i=1, 2,..M_j) available. Each individual method can be characterized by its effectiveness (e_{ij}), its extent of current use (u_{ij}), and its extent of further application or application potential (p_{ij}). The first parameter, effectiveness (e_{ij}), is defined as the measure of volume or toxicity reduction for a specific wastestream (j) due to full implementation of an identified source control method (i). The second parameter, the extent of current use (u_{ij}), is defined as the measure of the current level of use of the particular method to control a specific wastestream. Finally, the future application potential (p_{ij}), is a measure of probability that a given source control method will be implemented to control a specific wastestream. Such a variable depends on capital and operating cost, level of difficulty in implementation, implementation period, technological risk, and the risk of detrimental effects on product quality.

In mathematical terms, the current reduction index of the specific wastestream (j) by the implementation of the identified source control method (i) is given by:

$$(2) \quad c_{ij} = e_{ij}u_{ij}/S$$

Now that the current reduction index for each source control method has been calculated, the current reduction index for the wastestream (j) is given by:

$$(3) \quad C_j = c_{1j} + c_{2j}\,(1-(c_{1j}/S)) + c_{3j}\,(1-(c_{1j}/S) - (c_{2j}/S)(1-(c_{1j}/S))) + \cdots$$

The above equation shows that the current reduction index for a wastestream is equal to the reduction due to implementation of the first source control measure plus the reduction of the remaining waste due to implementation of the second source control measure and so on.

However, use of equation (3) can be unwieldly when a large number of control methods must be analyzed. In addition, estimates of C_j equal to 100 percent reduction will occur many times after accounting for the c_{ij}'s of only three or four methods. The problem is not with the equation however, but with the relative coarseness of the rating scale used (more accurate or quantitative data on percent effectiveness and extent of current use ratings would be required to use this equation). Therefore, using the single most effective applied control method (c_{ij} maximum) to represent the overall reduction achieved for a wastestream greatly simplifies the estimate while keeping it conservative (the actual reduction index should account for the most effective measure plus all of the other source control measures). Limiting C_j to a single most effective control method is given by the equation:

$$(3a) \quad C_j = \text{maximum } (c_{ij},\ i=1,2,\ldots M_j)$$

Now that C_j is determined for the wastestream, the current reduction index (C) for the process (all wastestreams) can be determined. Recalling that:

$$(1) \quad C = S\,(W_p - W_o)/W_p$$

the equation may be rewritten in terms of a single wastestream and rearranged so that:

$$(4) \quad W_{pj} = W_{oj}\,S/(S-C_j)$$

$$(5) \quad W_p = \sum_{j=1}^{N} W_{pj}$$

$$(5a) \quad W_p = \sum_{j=1}^{N} W_{oj}/(S-C_j)$$

To obtain the current reduction index C for the whole process (all waste streams), equations (5) and (1) are combined to yield:

$$(6) \quad C = S - W_o / \sum_{j=1}^{N} S\,(W_{oj}/(S-C_j))$$

Since it is usually easier to estimate the fraction of waste (Z_j) that a wastestream represents as part of the total waste generated (as opposed to estimating the actual waste generation rate), the following equations are used to calculate C:

$$(7) \quad Z_j = W_{oj}/W_o$$

$$(7a) \quad W_{oj} = W_o Z_j$$

$$(8) \quad C = S - 1/\sum_{j=1}^{N} (Z_j/(S-C_j))$$

The above equation relates the estimated current extent of waste reduction for the entire process to the current fraction Z_j of each process wastestream and to the current extent of waste reduction C_j for each wastestream.

Future Waste Reduction Index

In addition to the current reduction index C, an estimation of the potential future reduction index (F) is required. Individual future reduction indices (f_{ij}) for each control method can be calculated by using the equation:

$$(10) \quad f_{ij} = e_{ij}\,(S-u_{ij})\,p_{ij}/S^2$$

Now that individual future reduction indices for each source control measure are known, future reduction indices for each wastestream (F_j) can be determined. As was the case for the current reduction index, a conservative approach was used for

estimating the future reduction index of each wastestream. This approach assumed that industry would implement only a single source control method for each wastestream and not multiple methods.

The problem faced in this calculation is that it is even more difficult to predict which source control methods will be implemented in the future by individual facilities than to estimate the current levels of reduction. The variable F_j is subject to a high degree of uncertainty and is dependent on a number of factors including capital and operating costs, level of difficulty in implementation, implementation period, technological risk, and the risk of detrimental effects on product quality. Therefore, in estimating F_j, two different scenarios were assumed based on implementation of a single source control measure by industry.

The first scenario (F probable) assumes that industry as a whole will implement a range of methods. This implies that averaging of f_{ij}'s will yield a probable value of F_j:

$$(11) \quad F_j \text{ (probable)} = (1/M_j) \sum_{j=1}^{M_j} f_{ij}$$

This estimation of future reduction can be viewed as being a lower bound. The second scenario (F maximum) assumes that only the single, most effective method per wastestream will be implemented by industry. This implies that a conservative upper bound for F_j can be taken as:

$$(12) \quad F_j \text{ (maximum)} = \text{maximum } (f_{ij},\ i = 1,2,\ldots M_j)$$

Finally, for the entire process, the future probable and maximum waste reduction indices were taken as weight-fraction averages:

$$(13)\quad F_{probable} = \sum_{j=1}^{N} F_j\,(probable)\, Z_{oj}$$

$$(14)\quad F_{maximum} = \sum_{j=1}^{N} F_j\,(maximum)\, Z_{oj}$$

Future reduction indices F, expressed by equations (13) and (14) are qualitative measures of expected waste reduction from the process due to implementation of a range of methods for a given wastestream (F probable) or implementation of the single most effective control option for each wastestream (F maximum). Due to the need for two differing scenarios, the estimate of future waste reduction is presented as a range rather than a single value as shown for the current reduction index.

In summary, the method described above is based on an approach where the estimates of waste reduction were derived from the qualitative ratings based on engineering judgement given to the variables e_{ij}, u_{ij}, and p_{ij}. In actual applications however, it is usually not possible to obtain precise fractional values of e, u, and p. Instead, the variables were rated using an integer scale of zero to four. If this scale had to be converted into an equivalent range of percentages, then this range would approximately be:

Integer	Rating	Range, %
0	None	0-5
1	Low	5-35
2	Medium	35-65
3	High	65-95
4	All	95-100

Sample Calculation

The following steps are provided to guide the reader through the various calculations required in determining C and F. The first step required is to list all control methods by wastestream. Next, ratings are assigned to each method's effectiveness, extent of current use, and future application potential using the scale previously discussed (zero to four). In addition, fractional waste generation rates were assigned to each wastestream. As an example, see Table 3-1.

Now that the ratings and fractional waste generation rates have been assigned, calculations can begin. Using method #1, wastestream #1 as an example, the current reduction index for method #1 is computed using equation (2):

$$(2) \quad c_{ij} = e_{ij}u_{ij}/S$$

$$c_{11} = 2 \times 4/4 = 2.0$$

This calculation is repeated for all the methods. As a side note, the above calculation must be slightly modified whenever a current reduction index of 4 occurs (method #2, wastestream #2). The modification consists of restricting the maximum c value to 3.9 and not 4. This modification is required so that division by zero in equation (8) will not occur.

Now that the individual c values have been determined, the current reduction indices for the wastestreams are calculated using equation (3a):

$$(3a) \quad C_j = \text{maximum } (c_{ij}, i=1, 2,..M_j)$$

$$C_1 = \text{maximum } (c_{11}, c_{21}, c_{31}) = 2.0$$

$$C_2 = \text{maximum } (c_{12}, c_{22}, c_{32}) = 3.9$$

$$C_3 = \text{maximum } (c_{13}, c_{23}, c_{33}) = 1.5$$

TABLE 3-1 EXAMPLE SOURCE CONTROL METHODOLOGY TABLE

Waste Source	Control Methodology	Waste Reduction Effectiveness	Extent of Current Use	Further Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
							Probable	Maximum
Wastestream #1	1. Control method number 1.	2	4	0		2.0	0.0	
	2. Control method number 2.	4	0	1		0.0	1.0	1.0
	3. Control method number 3.	3	1	1		0.8	0.6	
	Overall	3.00	1.67	0.67	0.35	2.0	0.5	1.0
Wastestream #2	1. Control method number 1.	1	2	2		0.5	0.3	
	2. Control method number 2.	4	4	0		3.9	0.0	
	3. Control method number 3.	2	1	3		0.5	1.1	1.1
	Overall	2.33	2.33	1.67	0.20	3.9	0.5	1.1
Wastestream #3	1. Control method number 1.	2	1	1		0.5	0.4	
	2. Control method number 2	3	2	2		1.5	0.8	
	3. Control method number 3.	3	1	2		0.8	1.1	1.1
	Overall	2.67	1.33	1.67	0.45	1.5	0.8	1.1
All Sources	All Methods					1.00	3.6	0.6	1.1

and the current reduction index for the process is calculated using equation (8):

$$(8) \quad C = S - 1 / \sum_{j=1}^{N} (Z_j/(S-C_j))$$

$$C = 4 - \frac{1}{\frac{0.35}{4-2.0} + \frac{0.20}{4-3.9} + \frac{0.45}{4-1.5}}$$

$$= 4 - \frac{1}{0.175 + 2.0 + 0.18} = 3.6$$

To calculate the future reduction index for each method, equation (10) is used:

$$(10) \quad f_{ij} = e_{ij}(S-u_{ij})\, p_{ij}/S^2$$

$$f_{11} = 2 \times (4-4) \times 0/16 = 0.0$$

and so on. Then, the probable and future reduction indices are calculated for each wastestream using equations (11) and (12):

$$(11) \quad F_j(\text{probable}) = (1/M_j) \sum_{i=1}^{N} f_{ij}$$

$$F_1(\text{probable}) = (1/3) \times (0.0 + 1.0 + 0.6) = 0.5$$

$$(12) \quad F_j(\text{maximum}) = \text{maximum } (f_i,\ i=1,2,\ldots M_j)$$

$$F_1(\text{maximum}) = \text{maximum } (0.0,\ 1.0,\ 0.6) = 1.0$$

Finally, equations (13) and (14) are used to compute the overall future reduction indices for the process:

$$(13)\quad F(\text{probable}) = \sum_{j=1}^{M} F_j(\text{probable})\, Z_{oj}$$

$$F(\text{probable}) = 0.5 \times 0.35 + 0.5 \times 0.20 + 0.8 \times 0.45 = 0.6$$

$$(14)\quad F(\text{maximum}) = \sum_{j=1}^{M} F_j(\text{maximum})\, Z_{oj}$$

$$F(\text{maximum}) = 1.0 \times 0.35 + 1.1 \times 0.20 + 1.1 \times 0.45 = 1.1$$

1. PROCESS: ACRYLONITRILE (VINYL CYANIDE) MANUFACTURE

2. SIC CODE: 2869

3. INDUSTRY DESCRIPTION

The acrylonitrile manufacturing industry comprises facilities which tend to be part of large multiproduct corporations. In the U.S., the acrylonitrile industry is controlled by four large producers.

3.1 Company Size Distribution

Nearly all of the world's supply of acrylonitrile is manufactured by the ammoxidation of propylene using the Sohio Process. Plant capacities are large in order to take advantage of economics of scale. The total U.S. production capacity of the acrylonitrile industry in 1983 was 1,112,500 short tons. Plant capacity at the six U.S. acrylonitrile production facilities ranges from 132,500 to 230,000 short tons. Competition has reduced the number of acrylonitrile producers to the four companies listed in Table 3-1.

3.2 Principal Producers

There are four major producers of acrylonitrile:

American Cyanamid Company	Monsanto Co.
E.I. du Pont de Nemours & Co. Inc.	Standard Oil Company of Ohio

3.3 Geographical Distribution

Of the six plant locations listed in Table 3-1, four are located in Texas. Five of the establishments are located in EPA Region VI and one in Region V.

Table 3-1 Acrylonitrile Producers in the United States

Company	Capacity (short tons/yr.)	% of Total
American Cyanamid Co.		
Avondale, LA	132,500	11.9
E.I. du Pont de Nemours & Co.		
Beaumont, TX	175,000	15.7
Monsanto Co.		
Chocolate Bayou, TX	230,000	20.7
Texas City, TX	225,000	20.2
The Standard Oil Co.		
Lima, OH	150,000	13.5
Green Lake, TX	200,000	18.0
TOTAL	1,112,500	100.0

Source: Chemical Economics Handbook (SRI 1982) and industry comments.

4. PRODUCTS AND THEIR USE

The production of acrylonitrile increased rapidly during World War II due to the demand for its use in oil and solvent resistant rubber used for tires. Later, acrylonitrile became an integral raw material for fibers, synthetic resins, block copolymers, elastomers, and intermediates in organic synthesis (Groet 1979). Table 4-1 contains a breakdown of the uses of acrylonitrile.

Table 4-1 1984 Acrylonitrile Products and Use Distribution

Product	Percentage
Acrylic Fibers	44%
Acrylonitrile-Butadiene-Styrene (ABS) and Styrene-Acrylonitrile (SAN) resins	26%
Adiponitrile	14%
Acrylamide	7%
Nitrile Elastomers	3.5%
Others (including materials unaccounted for)	5.5%

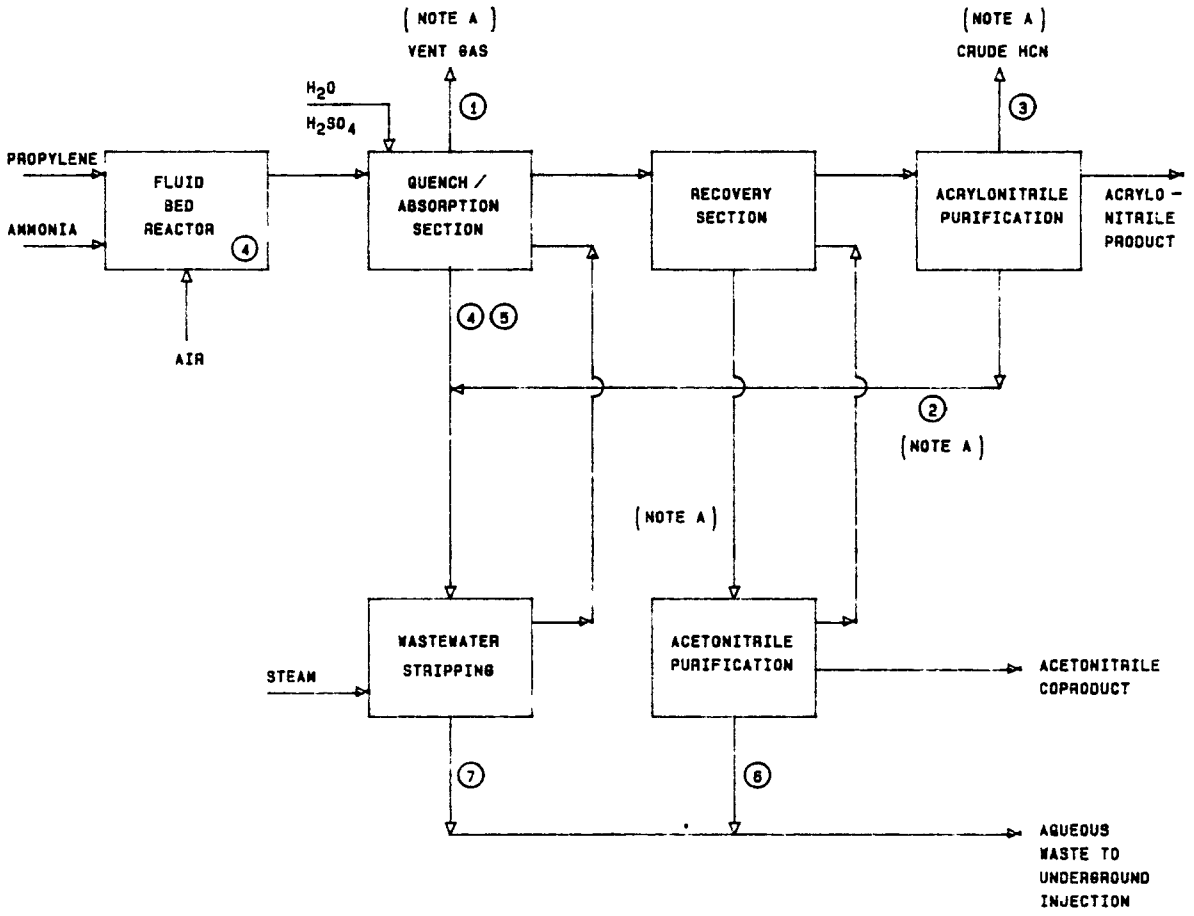
Source: Project staff estimates

5. RAW MATERIALS

The principal raw materials used to produce acrylonitrile are propylene, ammonia, and air.

6. PROCESS DESCRIPTION

The Sohio ammoxidation process (see Figure 6-1) is the most significant process route responsible for nearly 90 percent of the world's acrylonitrile production. In the Sohio ammoxidation process, propylene, ammonia, and air are exothermically reacted in a fluidized bed catalytic reactor at about 750-950^{o}F and 5-30 psig. The reaction may be represented as follows:



NOTE A. THESE STREAMS CAN BE INCINERATED

PROCESS WASTE CATEGORIES:

1. VENT GAS
2. AN PRODUCT COLUMN BOTTOMS
3. CRUDE HCN
4. SPENT CATALYST
5. ABSORBER EFFLUENT
6. ACE COLUMN BOTTOMS
7. WASTEWATER STRIPPER BOTTOMS

Figure 6-1 The Sohio Ammoxidation Process for Acrylonitrile Manufacture

$$2CH_2 = CHCH_3 + 2NH_3 + 3O_2 \xrightarrow{\text{catalyst}} 2CH_2 = CHCN + 6H_2O + \text{by-products}$$

The catalyst has been undergoing continuous improvement to produce higher yields of acrylonitrile. The early process version used a bismuth-phosphomolybdate catalyst, followed by introduction of antimony-uranium (catalyst 21) in 1967. A ferrobismuth-phosphomolybdate (catalyst 41) was introduced in 1972 boosting the capacity up to 35 percent. Currently, two catalysts are used: "Catalyst 49" with undisclosed composition and antimony-tellurium catalyst manufactured by Nitto Corporation.

A once through (non-recycle) reactor operation mode with a residence time of a few seconds is employed. Commercially recoverable quantities of acetonitrile (0.02 lb/lb propylene feed) and hydrocyanic acid (0.1-0.2 lb/lb propylene feed) are produced as by-products*. The reactor effluent is quenched and countercurrently scrubbed with a dilute sulfuric acid solution. The vent gas, primarily consisting of nitrogen with acrylonitrile, carbon oxides, propane, propylene, and trace amounts of acetonitrile and ammonia, is incinerated.

The organic-rich stream from the quench/absorption section is sent to the recovery section where crude acrylonitrile (AN) is separated and sent to the AN purification section to yield AN product, crude HCN stream and heavy-ends (AN product column bottoms).

Crude hydrocyanic acid (HCN) can be purified and sold or incinerated The AN product column bottoms are typically combined with the aqueous effluent from the quench-absorption section upstream of the wastewater stripping section (wastewater column). In some facilities, the AN product column bottoms are incinerated**.

The crude acetonitrile from the recovery section can be further purified or incinerated directly, depending on whether or not there is a commercial demand for it.

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* E.I. du Pont de Nemours & Co. 1985: Personal communication.

**Monsanto Co. 1985: personal communication.

The aqueous effluent from the quench-absorption section is typically comingled with the AN product column bottoms, steam stripped in the wastewater column, sent to the settling pond from which it is routed to underground injection. The wastewater stripper overhead is recycled back to the quench-absorption sections for organics recovery.

7. WASTE DESCRIPTION

The primary wastes evolved in the Sohio process are listed in Table 7-1. Generally, the undesirable heavy compounds formed as the result of side reactions during ammoxidation are separated as distillation column bottoms, combined with process water used to quench the reactor off-gas and absorb ammonia, and disposed of via underground injection.

Based on the information obtained, all operational facilities in the United States dispose of streams #2, 6 and 7 via underground injection. As mentioned before, stream #6 (ACE Column Bottoms) may not be produced by some facilities because of incineration of the crude acetonitrile. The constituents of these streams were reported as being not amenable to biological or chemical treatment (PRI 1977).

The disposal methods for minor wastes, such as spent catalyst, spills cleanup and equipment cleanup wastes could not be totally ascertained, although landfilling appears likely.

8. WASTE GENERATION RATES

The specific waste generation rates for selected waste streams from the Sohio process were given in terms of lb of waste/lb of product (PRI 1977) and are reported in Table 7-1. Overall waste generation rates for the manufacturing of acrylonitrile in the United States were unavailable. Fractional waste generation (percentage of waste each wastestream represents as compared to all waste generated) was estimated by the project staff based on available information and industry comments. These values are shown in Table 9-1.

Table 7-1 Wastes from Sohio Acrylonitrile Manufacture Process

No.	Description	Process Origin	Composition (lb/lb AN)	RCRA Codes
1.	Vent Gas	Quench-Absorption Section	Carbon Monoxide - .20 Propane - .05 Propylene - .02 Trace Organics & NH_3	____
2.	AN product column Bottoms	AN purification (AN Product Column)	High mol. wt. nitriles-and polymers-0.002 Acrylonitrile	K012 (delisted)
3.	Crude HCN	Lights column	HCN 0.1 Light Impurities	____
4.	Spent Catalyst	Reactor	Catalyst 49 or Nitto	____
5.	Wastewater	Absorber	Water-1.02 Ammonium Sulfate Acetonitrile- 0.02 Acrylomitrile HCN, solids	____
6.	Acetonitrile Column Bottoms	ACE Purification Section	Water Acetonitrile 0.02 Heavy ends 0.003	K013 K014
7.	Wastewater Stripper Bottoms	Wastewater stripper	See #2, 5 above	K011
8.	Spills & Leaks	Process Eqpt. & Piping	____	____
9.	Equipment Cleaning	Process Eqpt. Cleaning	____	____

9. WASTE REDUCTION THROUGH SOURCE CONTROL

This section deals with the problem of how to reduce the volumes and/or toxicities of the Sohio acrylonitrile process waste streams. The off-gas, HCN, and crude acetonitrile will not be considered in this report. Both HCN and crude acetonitrile are often incinerated. The off-gases, containing substances such as acetonitrile, HCN, propane, propylene, carbon monoxide, and acrylonitrile, are incinerated or catalytically abated.

9.1 Description of Techniques

The summary of source control methodologies is given in Table 9-1. Sections below deal with the description of the listed methods. In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" has also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel practices
  - management initiatives
  - employee training
- o Procedural measures
  - documentation
  - material handling and storage
  - material tracking and inventory control
  - scheduling
- o Loss prevention practices
  - spill prevention
  - preventive maintenance
  - emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Aqueous Waste to Underground Injection

This principal process waste stream is mostly water which contains low concentrations of ammonium sulfate, acrylonitrile, acetonitrile and heavier organic impurities which are formed as a result of side reactions. Generally, waste minimization can be addressed using four different approaches:

- Avoiding formation of undesirable byproducts in the reactor.
- Decrease of concentration of acrylonitrile (and acetonitrile) in the bottoms of their respective purification columns.
- Segregation and destruction of concentrated wastes (AN column bottoms and ACE column bottoms) instead of mixing them with the aqueous absorber effluent.
- Detoxification of aqueous waste.

The above measures would reduce the toxicity of the waste stream, but will not have a large impact on its volume. The volume reductions equate to reductions in water use and these can be addressed using the following approaches:

- Increasing concentration of sulfuric acid with the attendant decrease in water use.
- Use of a reboiler instead of steam in the wastewater stripper.
- Evaporation of water.

While these measures may reduce the volume of the ultimate waste, their effect on toxicity will be negative, i.e., the hazardous organics will tend to be more concentrated thus making the entire stream more toxic. For this reason, the principal

thrust of waste minimization should be toward toxicity reduction and the first four approaches indicated. The discussion of the specific measures identified for each approach is provided below.

9.1.1.1 Avoidance of Heavy Impurities Formation

This can be accomplished through the following measures:

- o Increase in catalyst selectivity toward AN formation.
  In the past, catalyst improvements have contributed significantly to the increase of AN yield with attendant decrease in the yields of ACE and heavier impurities. The research should be continued to develop more selective and stable catalysts.

- o Reduction of ammonia concentration along the reaction path.
  Literature indicates that some of the impurities are formed because of the excess ammonia present during the primary reaction (Jones 1971, Lurgi 1975). Conceptually a decrease in ammonia concentration in the reaction zone can lower the formation rate of the undesirable byproducts. The following avenues were identified.

  - staged NH_3 addition e.g. using multiple ring distributors or multiple beds.

  - direct quench of hot reactor offgas without heat recovery to minimize byproduct formation in the absence of catalyst contact.

- o Improved contacting between gas and catalyst in the ammoxidation reactor.
  According to present knowledge, the interchange rate of gas between the bubble and emulsion phase is diminished, as bubble size increases due to coalescence (Kunii & Levenspiel 1977). As a result, gas-to-catalyst contact is decreased, along with an attendant drop in product yield and an increase in by-product formation. It would follow that by keeping the effective bubble size small, the ammonia residence time in the emulsion phase (where most of the catalytic reaction takes place), will increase,

thus reducing ammonia bypassing along with by-product formation. The disadvantage is present in the decrease of the solid flux in the reactor with attendant drop of heat transfer rate. This can be overcome by using more heat transfer area or a cooler heat transfer medium. The bubble size can be controlled by cooling coil pitch, bed aspect (length-to-diameter ratio) and distributor design. It is suggested that consideration be given to all means of increasing the gas-to-catalyst contact.

o Rapid quench of the reactor off-gas.

The rationale behind proposing this method is that the by-product formation rate may be curtailed by limiting the time elapsed between the moment the reactor off-gas leaves the catalytic zone and the moment it is cooled down sufficiently to arrest the undesirable reactions. These reactions would occur in the interim when the gas is hot and not in the intimate contact with selective catalyst. The following specific measures are noted:

- installation of cooling coil in the freeboard space of the reactor.
- moving the cooler or venturi as close as possible to the reactor.
- elimination of cyclone in favor of an integral high temperature ceramic fiber filter to reduce freeboard space requirement.
- use of cooling jacket or radiator fins on the reactor exit piping.
- elimination of indirect cooling in favor of direct quench.
- use of cooler with low residence time (higher heat transfer rate).

o Raw material purification.

Most facilities that purchase their raw materials (as opposed to producing them), utilize standard (99.8% purity) grade ammonia and chemical grade propylene in the production of acrylonitrile. In principle, the generation of certain by-products, such as tars might be reduced by using a higher grade of feed-stock. Results from a test reactor study performed by DuPont, however, indicated that there was no difference in tars formation between a polymer grade and a chemical grade propylene feed*. The effect of ammonia purity was not established, although it is doubtful that it is significant.

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* E.I. du Pont de Nemours & Co. 1985: Personal communication.

Some of the above measures are purely suggestions which ultimately may or may not deserve an in-depth consideration, however, it is felt that a further assessment is warranted.

9.1.1.2 Decrease of AN and ACE concentrations in the purification column bottoms.

This approach will reduce the amounts of both compounds discharged with the principal waste stream. The decrease of AN or ACE concentration in the bottom stream means an increase of concentration of heavier impurities. In principle, this can be accomplished through additional distillation, e.g. an increase in the number of stages in the stripping section of both AN and ACE columns or secondary recovery.

9.1.1.3 Segregation and destruction of AN and ACE column bottoms.

Presently, these streams are mixed together with the aqueous effluent from the quench-absorption section (AN product bottoms upstream and ACE bottoms downstream of the wastewater column). By segregating these streams and their subsequent incineration at high temperature, the content of hazardous compounds in the discharged wastewater will be lessened. There are industrial precedents to incineration of both streams.

9.1.1.4 Detoxification of the aqueous waste.

Various approaches to the detoxification problem have been reported. Alkaline hydrolysis was in operation at Du Pont's now defunct Memphis facility, where a biodegradable effluent was produced and routed to a municipal sewer (Lowenbach and Schlesinger 1978). Inorganic compounds recovery from the wastewater was considered. The process developed by Erdolchemie recovers fertilizer grade ammonium sulfate (Groet 1979). Difficulties with metallic compound impurities (present because of catalyst metals carryover) and with control of crystal size make this process questionable; no one in the United States uses it.

9.1.2 Spent and Lost Catalyst

There are two causes of catalyst loss: attrition and deactivation. Attrition involves breakup of catalyst particles into fines which are elutriated out of the reactor ending up as solids leaving the process via wastewater column. Deactivation appears to be caused by loss of active metal from the catalytic sites due to volatilization (e.g. of molybdenum).

In comparison to the wastewater, these wastestreams are minor, yet they could be minimized by:

- Development of tougher, more attrition-resistant catalyst support.
- Lowering the frequency of high temperature upsets in the fluid bed.

9.1.3 Equipment Cleanup Wastes

Usually, the wasteloads associated with equipment cleaning are small and periodic in nature (once every 1 or 2 years). Further reductions may be obtained through:

- Provision of more drainage time before cleanup or steamout.
- Use of non-stick (electropolished or Teflon*) heat exchanger tubes to reduce deposit clingage (Anonymous 1985b).
- Use of in-process heat exchanger tube cleaning devices (Anonymous 1985a).
- Lower process film temperatures and increased turbulence at the heat exchange surfaces to reduce fouling rates.

*Registered trademark of E.I. du Pont de Nemours & Co.

9.1.4 Spills and Leaks

As mentioned before, spills and leaks constitute a very minor waste stream owing to extensive implementation of preventative maintenance measures in facilities dealing with hazardous materials. Further source reduction is possible, in principle, through better operating practices (see practice study entitled "Good Operating Practices"). Additionally, some consideration should be given to:

- Use of bellows-sealed valves.
- Replacing single mechanical seals with double mechanical seals on pumps or use of canned seal-less pumps.
- Use of leak detection systems and portable monitors.
- Enclosed sampling and analytical systems.
- Use of vapor-recovery systems for loading, unloading and equipment cleaning.

9.2 Implementation Profile

Some of the identified source control options may require extensive engineering and economic analysis before implementation. The four U.S. producers of acrylonitrile are large organizations with excellent technical capabilities. Therefore, analyses of technical and economic feasibility are best performed by their resident technical staff. No process-specific source control implementation avenues have been identified here.

9.3 Summary

Table 9-1 presents a summary of proposed source control methodologies. Each technique described in the text was rated using the input from industrial reviewers in three categories: effectiveness, extent of current use and future application potential. The ratings were combined into current and future reduction indices for each technique, waste stream and the entire process.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE ACRYLONITRILE MANUFACTURING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Aqueous Waste to Underground Injection (*)	1 Develop more selective catalyst	2	1	3	2	4		1.5	1 5	1 5
	2. Reduce ammonia concentration	1	1	1	0	1		0 0	0 3	
	3. Improve gas/catalyst contact	0	0	2	2	3		1.0	0 8	
	4. Quench reactor offgas rapidly	0	0	2	1	2		0.5	0.8	
	5. Purify raw material feed	1	2	1	1	1		0 3	0 2	
	6 Decrease AN/ACE conc in col bottoms	1	1	2	1	2		0.5	0.8	
	7. Segregate/destroy AN/ACE col bottoms	1	1	2	1	3		0 5	1.1	
	8 Detoxification of aqueous waste	1	1	1	0	2		0.0	0 5	
	Overall	0 88	0 88	1 75	1 00	2 25	0 96	1 5	0 7	1.5
Spent and Lost Catalyst	1 Develop tougher catalyst support	1	1	2	1	1		0.5	0.4	0.4
	2. Minimize reactor hot zone	1	1	1	0	1		0 0	0.3	
	Overall	1 00	1.00	1 50	0 50	1.00	0 01	0 5	0.3	0.4
Equipment Cleanup Wastes	1 Increase equipment drainage time	1	1	3	3	2		2 3	0.4	
	2. Lower heat exchanger film temperature	1	1	2	1	1		0.5	0 4	
	3. Electropolish heat exchanger tubes	2	1	3	0	2		0 0	1 5	1.5
	4 Use in-process H.X cleaning devices	2	1	2	1	2		0 5	0.8	
	Overall	1 50	1 00	2.50	1 25	1 75	0 02	2 3	0 8	1.5
Spills and Leaks	1 Use double mechanical seals on pumps	1	1	3	4	2		3 0	0 0	
	2 Use leak detectors	3	3	2	3	1		1.5	0.1	0 1
	3 Enclosed sampling and analy systems	3	2	2	3	1		1 5	0.1	0 1
	4. Use of vapor recovery systems	2	2	4	4	1		3.9	0.0	
	Overall	2 25	2 00	2 75	3.50	1.25	0 01	3 9	0 1	0.1
All Sources	All Methods						1 00	2 0	0.7	1.5

(*) These waste streams include listed "F" and/or "K" RCRA wastes

It appears that the currently achieved reduction of waste due to the present level of implementation of all methods listed is characterized by the current reduction index (CRI) of 2.0 (50 percent) on a scale of zero to four. This is a measure of how much waste was reduced with respect to the quantity that would have been produced if none of the methods listed were employed at their current level. High CRI value indicates that acrylonitrile producers have reduced their waste considerably.

It also appears that the future reductions are characterized by future reduction index of 0.7 to 1.5 on a scale of zero to four (18 and 38 percent respectively). This means that by implementing all listed techniques to their full rated potential, the current waste can be further reduced only to a moderate extent.

Many of the noted techniques were arrived at through engineering analysis of rather limited available process information and do require further evaluation. Among the techniques that appear especially worthy of further investigation (as evidenced by high individual future reduction index) are the improvement of catalyst selectivity and segregation and destruction of AN and ACE column bottoms.

10. PRODUCT SUBSTITUTION ALTERNATIVES

Today's major use of acrylonitrile is in the making of acrylic and modacrylic fibers. Acrylic fibers contain about 90% acrylonitrile. These fibers are essential in the production of various knit fabrics, carpets, blankets, draperies, upholsteries, felts fiberfils, hairpieces, industrial filtration systems, and paint roller covers. Due to the many uses of acrylic fiber, it's demand has been sharply increasing, thus, so has the demand for acrylonitrile.

In 1973, limitations on propylene supplies (the raw material used for producing acrylonitrile) began to occur. This, coupled with an increase in demand for acrylic fibers, led to an acrylonitrile shortage. The raw material shortage affected fiber producers in several ways. Textile mills began to place emphasis on increasing fabric yardage by producing lighter weight fabrics and on increasing production of the more profitable better quality fabrics (as opposed to more abundant low and medium priced ready-to-wear garments). This precedent indicates the possibility that fabric yardage can be extended.

11. CONCLUSIONS

The acrylonitrile industry appears to have reduced its waste generation rates considerably, in the range of 50 percent. The extent of future reductions of toxic components in all wastestreams appears moderate, in the estimated range of 18 to 38 percent.

Most of the identified techniques need further evaluation. Catalyst improvement and bottoms stream segregation and destruction appear to be most promising routes to minimize waste. The only product substitution alternative identified was fabric yardage extension.

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13. INDUSTRY CONTACTS

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1. PROCESS: AGRICULTURAL CHEMICAL FORMULATION AND APPLICATION
2. SIC CODE: 2879
3. INDUSTRY DESCRIPTION

The industry includes companies which formulate and prepare agricultural pest control chemicals or pesticides. This includes insecticides, herbicides, and fungicides. These products are formulated from pesticide concentrates manufactured elsewhere and are distributed to farmers in ready-to-use form.

3.1 Company Size Distribution

The industry is comprised of roughly 330 establishments nationwide. More than 64% of the establishments employ less than 20 people, although this group comprises only 7% of the total work force. A small number of large companies employ the majority of workers. Table 3-1 summarizes company size distribution.

Table 3-1 Company Size Distribution

	No. of employees per facility					
	Total	1-9	10-49	50-99	100-249	250+
No. of establishments	330	166	113	23	15	13
No. of employees	16,500	800	2600	1700	2200	9400

Source: 1982 Census of Manufacturers (USDC 1985).

3.2 Principal Producers

There are clearly no major producers which dominate the industry. Some formulation plants are owned by large pesticide manufacturers, while others are owned by independent formulators.

3.3 Geographical Distribution

The geographical distribution of establishments in the agricultural chemicals formulation industry is shown in Table 3-2 and Figure 3-1. Approximately 59% of

the establishments are located in 10 states, although no one state accounts for a major share of the industry. Most of the establishments are located near the agricultural areas which make use of the products.

Table 3-2 Location of Facilities by EPA Region

EPA Region	Number of Establishments[a]
I	-
II	33
III	-
IV	52
V	32
VI	37
VII	13
VIII	25
IX	43
X	5
National	240[b]

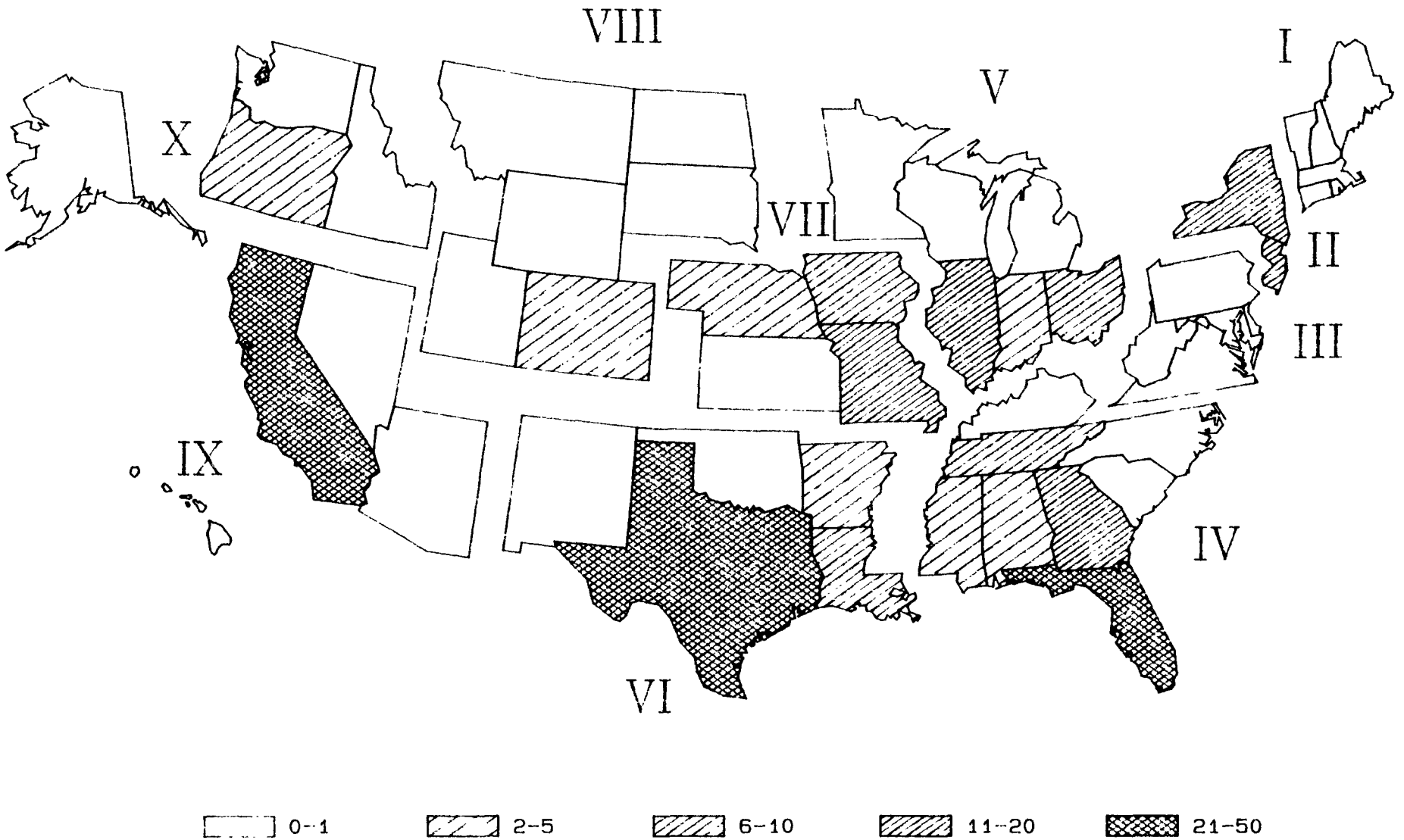
Source: 1982 Census of Manufacturers (USDC 1985)

[a] Includes only those establishments in states with 150 or more employees.

[b] The discrepancy between Table 3-1 and Table 3-2 is caused by the exclusion of establishments in states with less than 150 employees.

4. PRODUCTS

The agricultural chemicals industry (SIC 2879) produces pesticides and other agricultural chemicals not elsewhere classified, such as soil conditioners. This study is mainly concerned with pesticides. In the U.S., over 600 different pesticides are



Roman numerals show EPA regions

Figure 3-1 Pesticide Formulating Plants in the U.S.

produced (Kryeger 1983). Most pesticides can be classified as either insecticides, herbicides, or fungicides, although many other minor classifications exist. Table 4-1 below lists the production of the major classes of pesticides. Each division is subdivided according to chemical type.

Roughly 75% of all insecticides and herbicides, and 66% of all pesticides, are used on agricultural cropland. The remainder are used in private homes and gardens and on commercial and industrial property (Dillon 1981). The majority of pesticides are used on only a few major crops. Currently, cotton, corn, and apples receive 67% of all insecticides used in agriculture. Corn and soybeans receive 60% of the herbicides used, and 84% of the fungicides are applied to fruits and vegetables (Dahlston 1983). Only 48% of the total U.S. cropland is treated with pesticides (Dahlston 1983).

Table 4-1 1982 Pesticide Production in the U.S.

Product	Quantity Produced (tons per year)
Insecticidal formulations	
Inorganic compounds	54,300
Organic compounds	206,750
Chlorinated hydrocarbons	18,900
Carbamates	78,400
Organophosphates	73,150
Biological (botanical, bacterial)	11,250
Other organics	25,050
Herbicide formulations	
Inorganic compounds[a]	N/A
Organic compounds	541,750
Phenoxy	101,400
Metal organic	9,450
Triazine	97,250
Urea, Amide, Benzoic, other organics	333,150
Fungicide formulations	
Inorganic compounds[a]	N/A
Organic compounds	56,250
Other pesticidal formulations	
Fumigants	17,450
Defoliants and dessicants	3,500
All others[a]	N/A

Source: 1982 Census of Manufacturers (USDC 1985).
(a)Data not available.

5. RAW MATERIALS

As listed below, input raw materials include the pesticide concentrates from pesticide manufacturing plants as well as diluents and other chemical additives used in the formulating process (Metcalf 1981):

Pesticide Concentrates

Organic/Inorganic	Insecticides, herbicides, fungicides, others

Formulation and Preparation Materials

Dust Carriers	Organic flours, sulfur, silicon oxide, lime, gypsum, talc, pyrophyllite , bentonites, kaolins, attapulgite, volcanic ash
Solvents	Kerosenes, xylenes, methyl isobutyl ketone, amyl acetate
Others	Wetting and dispersing agents, masking agents, deodorants, emulsifiers

6. PROCESS DESCRIPTION

There are two major steps in the production of pesticides for agricultural use. The first step is the manufacturing of the pesticide concentrate from basic chemical feedstocks including petrochemicals, inorganic acids, gases such as chlorine, and other chemicals. This produces the pesticide, but not in a form which is ready for use. The second major step, which is the focus of this report, is the formulation and preparation of the pesticide for final use.

The formulation process depends on the desired form of the pesticide. Common pesticide formulations include dusts, wettable powders, emulsions, granules, and aerosols (USEPA 1979). Wettable powders are the most widely used formulation in agriculture. While each of these formulations is produced differently, the major unit

operations common to them all include the dry mixing and grinding of solids, dissolving or melting of solids into solution, and blending. A typical liquid pesticide formulation process is shown in Figure 6-1.

The application of pesticides to agricultural crops is an entirely separate operation, but is included here since it also results in the generation of pesticide wastes. The three major methods of pesticide application in agriculture are spraying (of liquid pesticides), dusting (of powders), and fumigation (of aerosols) (Metcalf 1981). Aerial spraying accounts for roughly two-thirds of all applications of pesticide in agriculture. Wastes are generated during the cleaning of the application equipment.

7. WASTE DESCRIPTION

The primary wastes from the formulation and application of pesticides along with their process origin and composition are given in Table 7-1. Pesticide formulations are generally produced in a batch mode. As a result, the same formulating equipment is often used to produce a variety of products. This results in the need to clean the process equipment prior to every product switch-over in order to prevent contamination between batches. The resulting cleaning wastes account for a substantial amount of the waste produced during pesticide formulation. The cleaning wastes may be either aqueous or organic liquids, or solid materials such as powders or granules, depending on the type of pesticide being formulated.

Used drums, bags, and other packaging material may contain up to several ounces of pesticides or other raw materials, thus becoming an additional waste source. Other wastes produced during the formulation process include spills, off-specification batches of pesticides, and air pollution scrubber wastewater (Gruber 1975). Poor process control often results in the production of off-specification material. This is either disposed of as a waste, or recycled within the process and upgraded to an acceptable quality.

The application of pesticides to crops also results in waste generation. As in the formulation process, sprayers and other application equipment are often used to apply more than one product. The equipment is usually cleaned between applications of

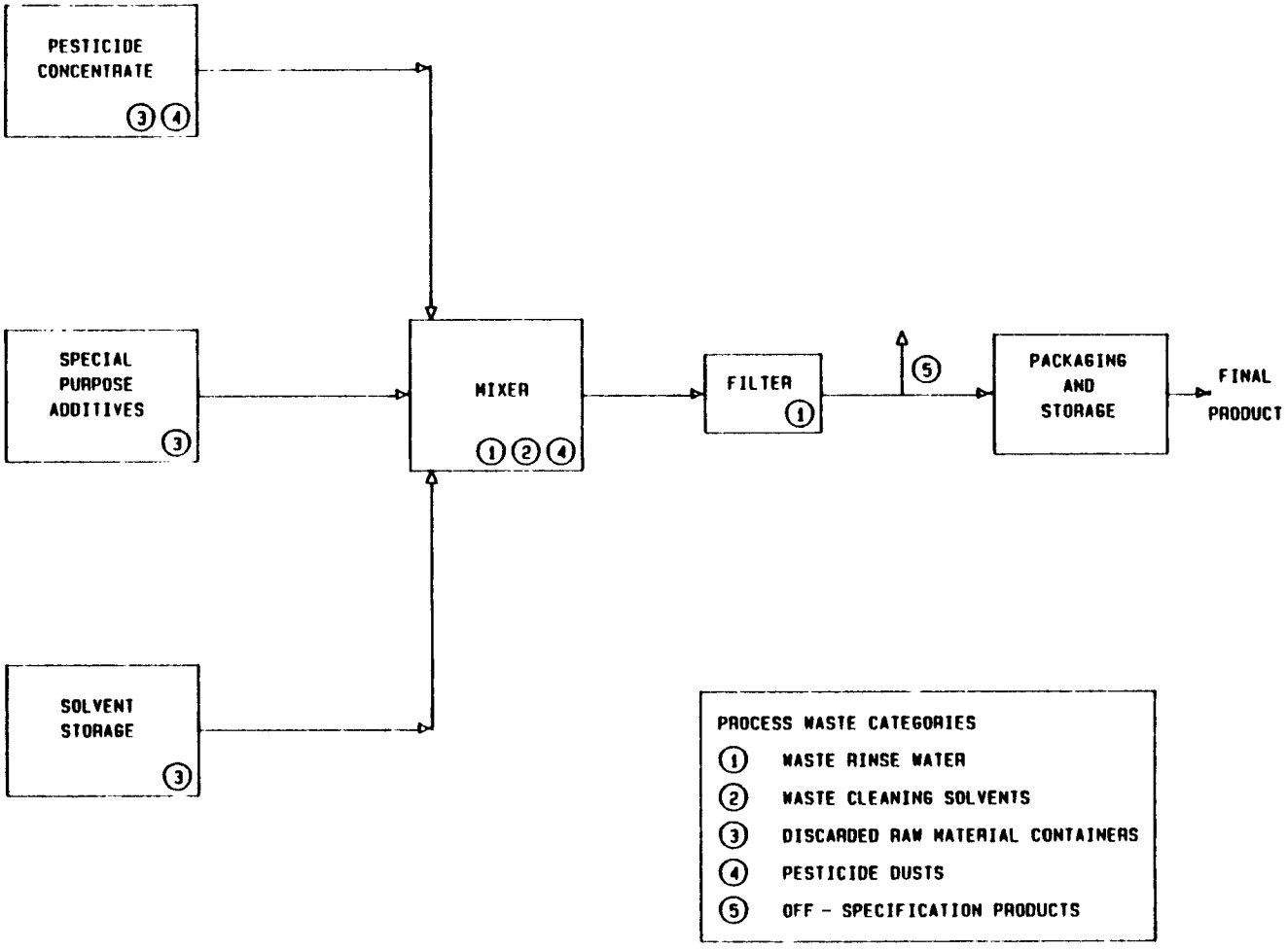


Figure 6- 1 Liquid Pesticide Formulation Process

Table 7-1 Pesticide Formulating Process Wastes

No.	Waste Description	Process Origin	Composition	RCRA Codes
1.	Waste rinse water	Equipment cleaning, spills, area washdown	Dissolved organics, suspended and dissolved solids.	--
2.	Waste solvents	Equipment cleaning, spills	See Section 5.	F002 F003
3.	Leftover raw materials	Raw material containers	Bags, fiber drums, steel drums with small amounts of residual raw material.	--
4.	Pesticide dust	Air pollution equipment	Pesticide dust, inert carrier dust. See Section 5.	--
5.	Off-specification products	Formulating	See Section 5.	--
6.	Scrubber water	Air pollution equipment	Dissolved organics, suspended and dissolved solids.	--

different chemicals to prevent cross contamination. The cleaning wastes produced are similar to those produced in the formulation process.

Evaporation is the most popular method of wastewater disposal at formulation plants (USEPA 1976). An evaporation system consists of a pit lined with concrete or an impervious plastic liner, and it may be heated or have a transparent cover to keep out rainfall. Spray irrigation has also been used to dispose of wastewater at some plants (USEPA 1976). Spray irrigation is sometimes limited by climatic conditions, necessitating disposal of the wastewater to a sewer during certain periods of the year. Rinse water from the cleaning of application equipment can be applied to land. This is a permissible practice under FIFRA and many individual farmers do it routinely.

8. WASTE GENERATION RATES

Very little data was available on specific waste generation rates from agricultural chemical formulation and application operations. In 1975, it was estimated that 0.0033 pounds of waste per pound of pesticide formulated was produced (Gruber 1975). This rate did not include waste from application of the pesticide. More recently, the nationwide waste generation rate (which includes waste produced during the cleaning of pesticide application equipment) was estimated to be over 100 million gallons per year (Dillon 1981). These wastes were mostly very dilute (less than 500 ppm) pesticide solutions, the large majority of which originated from the cleaning and washing of equipment and containers. Fractional rates have been estimated by the project staff based on best available information and engineering judgment and are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

The various wastes produced during the formulation and application of pesticides are shown in Table 7-1. The available methods of reducing waste production through source control can generally be grouped as either process modification methods or as those belonging to the group known as good operating practices.

Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel practices
  - management initiatives
  - employee training
- o Procedural measures
  - documentation
  - material handling and storage
  - material tracking and inventory control
  - scheduling
- o Loss prevention practices
  - spill prevention
  - preventive maintenance
  - emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Equipment Cleaning Wastes

Most of the wastewater produced at pesticide formulation plants results from the cleaning of process equipment. As noted earlier, a typical formulation plant produces a variety of different pesticides, all on a batch basis. Between batches, the mixing tanks and all other equipment exposed to the pesticide must be cleaned to avoid contamination between different products.

If powders or other "dry" pesticides are formulated, then cleaning is accomplished using a dry, inert material, such as clay. If liquid pesticides are formulated, cleaning is normally performed by rinsing with water. More than one rinse is usually required to adequately clean a tank. The following waste reduction methods are noted:

- o Storage and reuse of rinse water and other cleaning wastes.
  Many plants collect and store rinse water from equipment cleaning and reuse it as make-up water during the next formulation of the same product

(USEPA 1976). This greatly reduces wastewater generation, in addition to allowing for product recovery. This idea has also been used in the formulation of solvent-based products. One plant cleaned all of their equipment with solvent, which was then collected and reused in the next compatible batch formulation (USEPA 1976).

If it is not practical to use the waste rinse water as make-up during a later formulation, it can be reused as rinse water. In those instances where more than one rinse is needed to clean the equipment, the first rinse can be performed using old rinse water from a previous formulation. This rinse will remove the bulk of the pesticide residue from the equipment, then a second rinse with fresh water can be used to complete the cleaning.

- Use of high pressure spray nozzles.
  High pressure spray nozzles can be used in place of the standard rinsing hoses. According to a study of equipment cleaning in the paint industry (USEPA 1979), water consumption can be cut by 80-90% when high pressure rinsing systems are used.

For additional information and examples of low-waste approaches to equipment cleaning, the reader is referred to the study of process equipment cleaning in this appendix.

9.1.2 Spills and Area Washdowns

The cleanup of spills and area washdowns often contributes significantly to the total waste volume produced at formulation plants. Spills are caused by the accidental discharge of pesticides during transfer operations or from equipment failures such as leaks. Area washdowns with water hoses are performed routinely at some formulation plants, and are necessary in the event of contamination of the working area (USEPA 1976). Waste reduction methods available for these wastes include the use of dry cleanup methods for spills. Rather than cleaning spills with water and discharging the water to the sewer, many formulating plants use dry absorbents for spill cleanups

(USEPA 1976). This greatly decreases the waste volume associated with the cleanup. In addition, floor sweeping can be used to collect spills for product reformulation. Such practice was reportedly performed by Chevron Chemical Co. to reduce their waste generation volume (LWVM 1985).

9.1.3 Off-Specification Products

Off-specification batches of pesticide formulations are produced as a result of poor process control and operation. Ideally, this waste source could be eliminated totally by making use of the following source control techniques:

- Strict quality control and process automation
  The formulation of pesticides is a relatively simple process. Nevertheless, process automation and control during formulation ensures repeatable high quality products and avoids generation of off-spec batches due to operator error.

- Reformulation of off-specification batches
  If a batch of off-specification pesticide is produced, it should be reformulated to an acceptable quality rather than discarded as a waste.

9.1.4 Packages and Drums

Drums or other packaging materials contribute to the waste output from a formulating plant. After the drums, which are used to store or transport pesticides, are emptied, a small amount of pesticide residue remains. To clean the drums, it is necessary to rinse them with water or use an inert solid, such as clay. Thus, additional cleaning waste is generated. If the drums and packaging material are not cleaned or decontaminated, then they must be treated and disposed of as a waste. Some formulation plants sell used drums to a drum reconditioner, while others reuse them internally. There is thus a tradeoff between disposing uncleaned drums as a waste, and producing a waste by cleaning them. From a waste reduction standpoint, both of these methods should be considered, and the most efficient method should be chosen on a plant by plant basis.

As an example, Chevron Chemical Co. combined the use of water conservation techniques in triple-rinsing pesticide containers to be returned to the manufacturers. This practice reduced approximately 50% of the containers discarded. In addition, non-returnable pesticide-containing drums were replaced by returnable bulk tote bins to reduce the overall waste generation amount (LWVM 1985).

9.1.5 Dust From Air Pollution Equipment

Dusts generated during handling, grinding, and other formulation operations are a potential waste source. It is common practice to install dust collection equipment, such as hoods served by a baghouse filter, on all dust-generating operations. This allows for the recycling of the dust, thereby reducing waste production and decreasing worker exposure to hazardous substances (USEPA 1976). For example, Daly-Herring Co. reportedly altered their dust collection equipment operation so that waste streams containing organic chemicals from various production areas were collected separately rather than mixed in a single baghouse. The uncontaminated streams collected were recycled to the processes where they were generated (Huisingh et. al. 1985).

9.2 Implementation Profile

The major thrust of source control in the pesticide formulation process should be towards reduction of the principal waste stream, i.e. equipment cleaning wastes. The two methods identified are the storage and reuse of rinse water and other cleaning wastes, and the use of high pressure spray systems. Storing cleaning wastes for future reuse would require the establishment of a storage area with tanks, pumps, piping and instrumentation. The installation of a high pressure spray system would require a spraying unit, pump, and piping at each cleaning area. The space requirements for such a system would not be large. Both of these source reduction measures would require a capital expenditure. This expense would be offset by the savings in wastewater treatment due to the smaller volumes of waste produced.

9.3 Summary

The waste sources and the associated source control techniques are summarized in Table 9-1. The ratings listed in this table are based on a scale of 0 to 4 and are used

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE AGRICULTURAL CHEMICALS FORMULATION INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality	Effectiveness					Probable	Maximum
Equipment Cleaning Wastes (*)	1 Reuse waste rinsewater/solvent	3	3	3	3	3		2.3	0 6	
	2. Use high pressure sprays	1	3	3	2	3		1.5	1.1	1 1
	Overall	2 00	3 00	3 00	2.50	3 00	0 60	2.3	0 8	1 1
Spills and Area Washdowns	1. Better operating practices	1	1	3	3	2		2 3	0 4	
	2 Use of dry clean up methods	2	2	2	2	2		1 0	0 5	0 5
	Overall	1.50	1.50	2.50	2 50	2 00	0 05	2 3	0 4	0 5
Off-Spec Products	1. Quality control/automation	1	1	3	2	2		1 5	0.8	0 8
	2 Reformulation of off-spec batches	2	2	3	3	2		2 3	0 4	
	Overall	1 50	1.50	3 00	2 50	2 00	0.05	2 3	0 6	0 8
Packages and Drums	1 Clean and re-use	1	2	3	1	3		0 8	1 7	1 7
	Overall	1 00	2 00	3.00	1 00	3 00	0 25	0 8	1 7	1 7
Dust /Air Pollution Equipment	1. Collect dust and reuse	1	2	3	3	1		2.3	0.2	0 2
	Overall	1 00	2 00	3 00	3 00	1 00	0.05	2.3	0.2	0 2
All Sources	All Methods						1 00	2 0	1 0	1.2

(*) These streams include listed "F" and/or "K" RCRA wastes

to evaluate each technique for its waste reduction effectiveness, extent of current use, and future application potential. The ratings were derived by project staff based on a review of the available information.

It appears that the current level of waste minimization in the pesticide formulation industry is relatively high, as evidenced by the current reduction index (CRI) of 2.0 (50 percent). CRI is the measure of waste reduction achieved due to the current application level of all the techniques listed.

Any future reductions of waste generation appear to be moderate as characterized by the future reduction index (FRI) of 1.0 to 1.2 (25 to 30 percent). FRI is the measure of waste reduction achievable through implementation of the listed techniques to their full rated potential. The most effective measures for achieving this reduction involve reusing waste rinse water, using high pressure spray systems, using dry cleanup methods for spills, increasing the use of automation, and reusing empty drums.

10. PRODUCT SUBSTITUTION ALTERNATIVES

The discussion has, so far, been concerned with reducing the wastes associated with the formulation of pesticides. While this is a valid concern, this approach does not consider the hazards associated with the pesticides themselves. The wastes produced during the formulation process are basically dilute pesticide solutions and off-specification pesticide formulations. These are often no more hazardous than the pesticide formulations being produced. Therefore, since pesticides are hazardous substances themselves, it is of major importance to evaluate safer, substitute products.

Pesticides represent only one means by which to protect agricultural crops from insects and other pests. Many other methods of crop protection exist which do not rely solely on the use of man-made chemicals. Integrated Pest Management (IPM) is an ecologically-based pest control strategy involving a variety of control methods. Pests are defined here as organisms which interfere with the production of agricultural crops. Pests include insects, diseases, parasites, and weeds.

The main underlying principle of IPM is that no single control method can be effective over the long term because of the adaptive powers of insects and other pests. The goal of IPM is not to eradicate pest populations, but rather to keep them just below the level at which the loss is deemed economically acceptable. The pest control methods used in an IPM program include (Bottrell 1979):

- Biological control

  Natural enemies such as parasites, predators, and diseases are used to regulate and balance pest populations. For example, if no natural enemies of a pest exist on a farm, farmers can purchase insects from insectaries and introduce them onto the farm (Smith 1985). This form of control is of major importance in IPM.

- Genetic control

  The breeding of plant species which are resistant to certain diseases or insects is highly effective and is used widely today. The large majority of U.S. cropland is currently planted with crop varieties which are resistant to, at least, one disease.

- "Cultural" control

  Cultural control of pests include farming practices such as land cultivating crop rotations, and strategic timing of planting, irrigation, and harvesting of crops. These practices can be used to prevent the proliferation of many pests.

- Chemical control

  Chemical control using pesticides is also an important part of IPM. Pesticides are applied only when absolutely necessary and in small amounts in order to keep pest populations from rising above the threshold level where they cause economic loss. The selective use of pesticides also avoids the needless destruction of parasites, predators, and diseases that can aid in the control of a pest population.

IPM has been used successfully on many farms to date, reducing pesticide use by 50-90% while maintaining crop yields (Metcalf 1981, Bottrell 1979). Since IPM is an

ecologically-based control strategy, each farm requires the development of its own program. While IPM has been used for the past two decades with much success, it is not being used extensively today. Several barriers exist which have hindered its widespread use. These include:

- Lack of knowledge

  Implementing an IPM program requires extensive scientific knowledge of the crop and its surrounding ecosystem. Growth characteristics of both the crop and its pests, as well as their interrelationships, must be understood. Such knowledge is often lacking and is difficult to establish.

- Lack of trained IPM personnel

  Before a farmer can begin an IPM program, an IPM specialist must be contacted. Since IPM requires extensive scientific information, the average farmer is dependent upon the help of an expert. Such experts are in short supply and are often unavailable. In contrast, there

- Farmers' attitudes

  Farmers are often skeptical of incorporating IPM into their farming practices. Those who have had much success with using pesticides as their primary means of pest control see no reason to change over to IPM.

- Lack of incentives

  IPM has been used successfully on many farms, drastically reducing pesticide consumption (Metcalf 1981, Bottrell 1979). Nevertheless, it has not yet gained widespread popularity; pesticides continue to be the primary means of protecting many crop from pests. The major advantages of IPM over current pesticide use are mainly environmental. There does not appear to be a general consensus concerning the economic benefits of IPM compared to traditional chemical methods of pest control. It is not clear whether or not IPM is economically advantageous.

  One method which has been proposed to decrease pesticide use is to lower the appearance standards set on food (Dahlston 1983). The current demands on such appearance qualities as color of fruits and vegetables in

the U.S. prohibits many farmers from adopting IPM, which often results in food of lower cosmetic quality compared to food produced using pesticides.

11. CONCLUSIONS

Several methods of reducing the waste generated during the formulation of pesticides are available. it is estimated that the total waste output could be moderately reduced by implementing the source reduction methods discussed. The most effective methods available for waste reduction are reusing waste rinse water and other cleaning media, using high pressure spray systems for equipment cleaning, and incorporating dry cleanup methods for spills.

The greatest environmental concern stemming from the use of pesticides is the toxicity of the pesticides themselves. Concern over the wastes associated with pesticide production is of secondary importance. This is evident from incidents in the past concerning the contamination of water supplies with pesticides, the build up of pesticides in the food chain, and farm workers' exposure to pesticides.

The use of pesticides on some farms has been greatly reduced by the use of Integrated Pest Management (IPM). IPM does not eliminate the use of pesticides, but reduces their consumption rate by placing more emphasis on natural and biological pest control methods.

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13. INDUSTRY CONTACTS

Confidential source.

1. PROCESS: ELECTROPLATING

2. SIC CODES: 3471

3. INDUSTRY DESCRIPTION

Electroplating is a process by which a metal object is coated with one or more thin layers of another metal by means of an electrical current, in order to alter the surface characteristics of the object. The electroplating industry is generally divided into two major segments: job shops which process materials owned by others on a contract basis and captive shops owned by larger manufacturing facilities.

3.1 Company Size Distribution

There were an estimated 13,000 job and captive electroplating shops in the United States (USEPA 1979). Roughly 69% of these are small captive shops which employ less than 20 people. Table 3-1 summarizes the industry size distribution for job shops; specific size distribution for captive shops is unknown.

Table 3-1 Company Size Distribution for U.S. Electroplating Job Shops in 1982

	No. of employees per facility				
	Total	1-19	20-49	50-99	100+
No. of establishments	3,450	2,394	725	230	101
No. of employees[(a)]	61,900	13,080	21,750	14,950	12,120

Source: Dunn's Marketing Services (1983), 1982 Census of Manufactures (USDC 1985)

(a) Breakdown of total was approximated from number of establishments and corresponding company size.

3.2 Principal Producers

The industry is dominated by small captive shops with less than 20 employees each. Thus, there are no major producers with a very large share of the entire market.

3.3 Geographical Distribution

The geographical distribution of electroplating shops is shown in Figure 3-1. As seen, the highest concentration of shops are in California, the Midwest, and the East Coast. The EPA regional breakdown is given below in Table 3-2.

Table 3-2 Geographical Distribution of U.S. Electroplating Industry by EPA Region

EPA Region	Number of Establishments
I	343
II	415
III	137
IV	208
V	1088
VI	190
VII	69
VIII	negligible
IX	615
X	32
Total	3103[a]

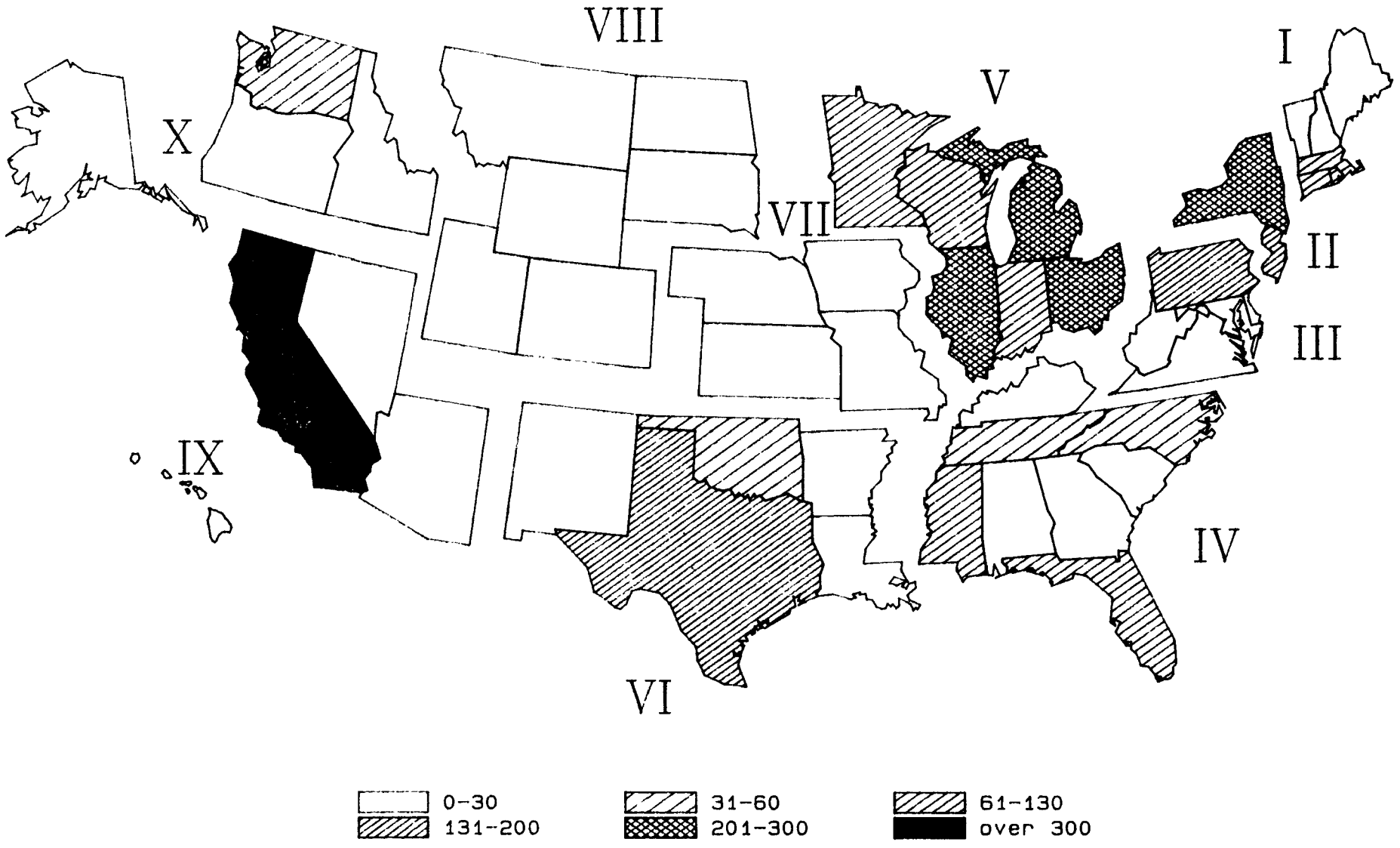
Source: 1982 Census of Manufacturers (USDC 1985).

(a) The discrepancy between Table 3-2 and Table 3-1 is caused by exclusion of states with less than 150 employees.

4. PRODUCTS

Principal product areas in which electroplating processes are involved include:

- automotive exterior/interior parts
- boat hardware
- plumbing fixtures
- cabinet hardware
- hydraulic cylinders
- shafts
- bearings
- seals



Roman numerals show EPA regions

Figure 3-1 Electroplating Plants in the U.S.

Products (Continued)

kitchen appliances	solar heated panels
utensils	defense hardware
tools	computer chassis
valve trim	printed circuit boards

5. RAW MATERIALS

Raw materials used in the electroplating industry include cleaning agents, plating solutions and metal anodes. Nationwide plating metal consumption rates are shown in Table 5-1 for selected metals.

Table 5-1 1982 Consumption of Metals by U.S. Electroplating Industry

Metal	Consumption (metric tons/yr)
tin	11,434
nickel	20,889
silver	123
gold	14.5
cadmium	971
zinc	342,044[a]
copper	no data

Source: 1982 Minerals Yearbook (USDC 1982).

[a] Includes hot dip galvanizing.

6. PROCESS DESCRIPTION

Electroplating is a process in which metal is coated with one or more other metals by electrodeposition. Electroplating is used to increase the corrosion resistance of a metal, to improve or alter the appearance of a metal, or to otherwise create a product which serves some useful end.

Electrodeposition is achieved by passing an electric current through a solution containing dissolved metal ions as well as the metal object to be plated. The metal object becomes a cathode in an electrochemical cell, resulting in the deposition of the

dissolved metal ions onto the surface of the metal object. Ferrous or nonferrous objects are commonly electroplated with aluminum, brass, bronze, cadmium, chromium, copper, iron, lead, nickel, tin, and zinc. Precious metals such as gold, platinum, and silver are also used widely.

The following processes are specifically excluded from this study since they are covered in other studies of this report:

- o Electronic Circuit Board Manufacturing
- o Anodic Oxidation
- o Electroless Plating

An electroplating process generally calls for moving the object to be coated (workpiece) through a series of baths arranged in a sequence designed to produce the desired end product. Typically, the sequence consists of cleaning, rinsing, and a number of alternating electroplating and rinsing steps. The workpiece can be carried on racks or in barrels. Large parts to be plated are mounted on racks which transfer the workpiece from bath to bath. If many small parts are to be plated, they can be contained in barrels which rotate in the plating bath. As an example, a flow chart of a chromium plating operation is shown in Figure 6-1 (Tavlarides 1982). A number of excellent detailed process descriptions are available (ASM 1964, Lowenheim 1979).

Electroplating produces a large variety of wastes, as discussed in Section 7. Most of the wastes produced contain metals and other compounds used in the various plating baths. Table 6-1 lists the constituents of the most commonly used plating baths.

7. WASTE DESCRIPTION

The ten primary electroplating process wastes and their respective points of origin and composition are listed in Table 7-1. The wastes produced at a particular plant will be similar to those listed, but their precise composition will depend upon the specific process employed. Some or all of the ten waste types may be combined into a single stream before treatment and disposal. It is common to combine the highly-concentrated cyanide wastes from the plating and cleaning solutions with filter sludges. These are kept separate from the acidic wastes and from the dilute cyanide solutions.

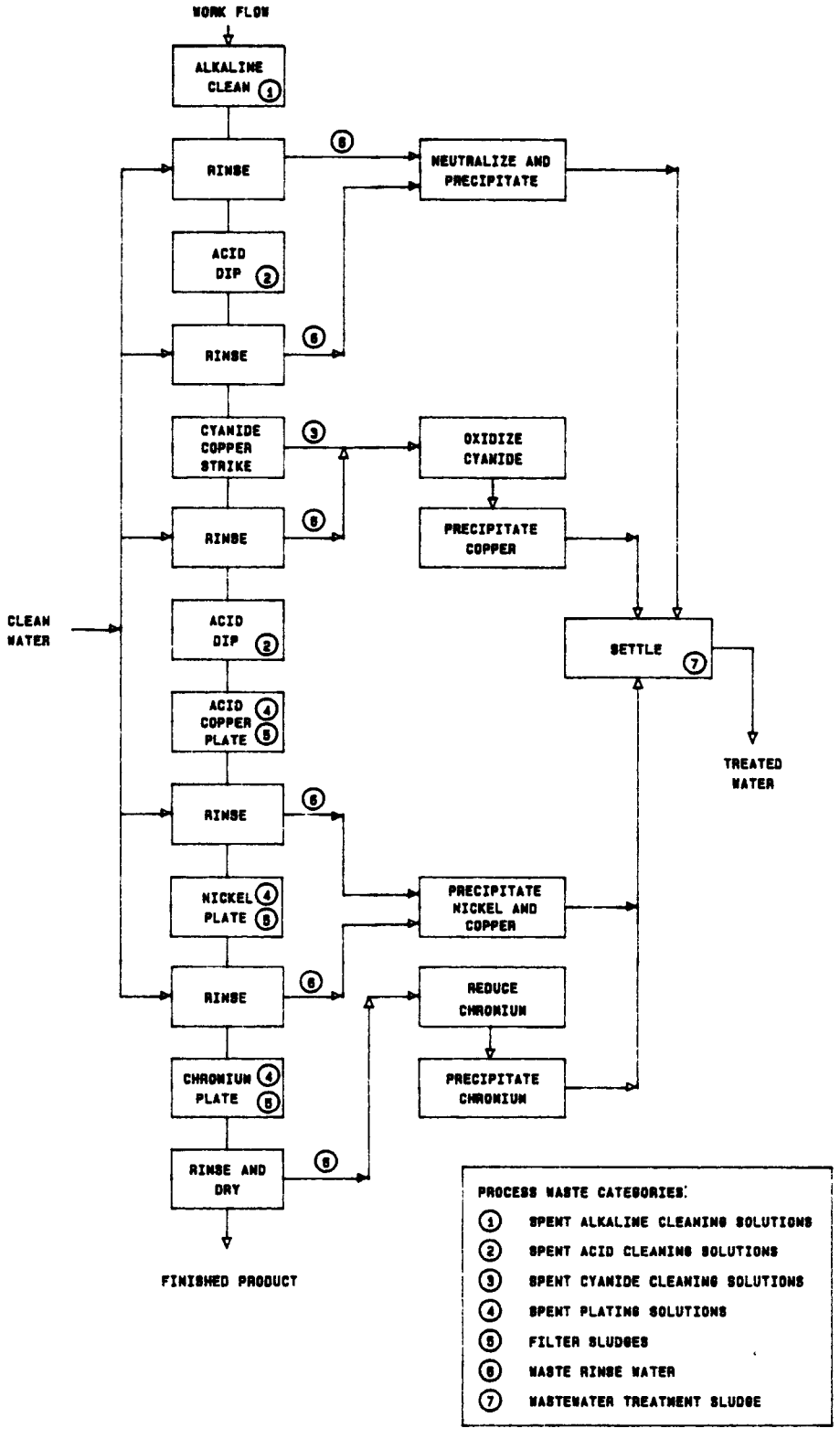


Figure 6-1 Block Flow Diagram for Chromium Plating Operation

Table 6-1 Common Electroplating Bath Compositions

Electroplating Bath	Composition
Brass & Bronze	Copper cyanide Zinc cyanide Sodium cyanide Sodium carbonate Ammonia Rochelle salt
Cadmium Cyanide	Cadmium cyanide Cadmium oxide Sodium cyanide Sodium hydroxide
Cadmium Fluoroborate	Cadmium fluoroborate Fluoroboric acid Boric acid Ammonium fluoroborate Licorice
Copper Cyanide	Copper cyanide Sodium cyanide Sodium carbonate Sodium hydroxide Rochelle salt
Copper Fluoroborate	Copper fluoroborate Fluoroboric acid
Acid Copper Sulfate	Copper sulfate Sulfuric acid
Copper Pyrophosphate	Copper pyrophosphate Potassium hydroxide Ammonia
Fluoride Modified Copper Cyanide	Copper cyanide Potassium cyanide Potassium fluoride
Chromium	Chromic acid Sulfuric acid
Chromium with Fluoride Catalyst	Chromic acid Sulfate Fluoride

Table 6-1 (continued)

Electroplating Bath	Composition
Gold Cyanide	Metallic gold Potassium cyanide Sodium phosphate
Iron	Ferrous sulfate Ferrous chloride Ferrous fluoroborate Calcium chloride Ammonium chloride Sodium chloride Boric acid
Lead Fluoroborate	Lead fluoroborate Fluoroboric acid Boric acid Gelatin or glue Hydroquinone
Lead-Tin	Lead fluoroborate Tin fluoroborate Boric acid Fluoroboric acid Glue Hydroquinone
Nickel (Watts)	Nickel sulfate Nickel chloride Nickel fluoroborate Boric acid Nickel sulfate Nickel chloride Nickel sulfamate Boric acid Phosphoric acid Phosphorous acid "Stress-reducing agents"
Nickel-Acid Fluoride	Hydrofluoric acid Nickel carbonate Citric acid Sodium lauryl sulfate (wetting agent)
Black Nickel	Nickel ammonium sulfate Nickel sulfate Zinc sulfate Ammonium sulfate Sodium thiocyanate

Table 6-1 (continued)

Electroplating Bath	Composition
Silver	Silver cyanide Potassium cyanide or Sodium cyanide Potassium carbonate or Sodium carbonate Potassium hydroxide Potassium nitrate Carbon disulfide
Acid Tin	Tin fluoroborate Fluoroboric acid Boric acid Stannous sulfate Sulfuric acid Cresol sulfonic acid Beta naphthol Gelatin
Stannate Tin	Sodium stannate Sodium hydroxide Sodium acetate Hydrogen peroxide
Tin-Copper Alloy	Copper cyanide Potassium stannate Potassium cyanide Potassium hydroxide Rochelle salt
Tin-Nickel Alloy	Stannous chloride Nickel chloride Ammonium bifluoride Sodium fluoride Hydrochloric acid
Tin-Zinc Alloy	Potassium stannate Zinc cyanide Potassium cyanide Potassium hydroxide
Acid Zinc	Zinc sulfate Ammonium chloride Aluminum sulfate or Sodium acetate Glucose or Licorice
Zinc Cyanide	Zinc oxide Sodium cyanide Sodium hydroxide Zinc cyanide

Table 7-1 Electroplating Process Wastes

No.	Waste Description	Process Origin	Composition	RCRA Codes
1.	Spent alkaline cleaning solution	Aqueous cleaning	$NAOH, Na_2CO_3, Na_2SiO_3, Na_3PO_4, Na_2HPO_4 (NaPO_3)_4$, cyanide, soils, EDTA+ Mg/Ca, saponified and/or emulsified grease	F009
2.	Spent acid cleaning solutions	Acid pickling	$HCl, H_2SO_4, HNO_3, H_2CrO_4, H_3PO_4, HBF_4, Me^+$, oils, soils	--
3.	Degreaser sludges	Solvent cleaning	kerosene, naphtha, toluene, ketones, alcohols, ethers, halogenated hydrocarbons, oils, soils, water	F001, F002 F003, F005
4.	Solvent recycle still bottoms	Solvent recycling	same as above solvents. May contain HCl from solvent decomposition	F001, F002 F003, F005
5.	Spent plating solutions	Electroplating	see Table 6-1	F007
6.	Filter sludges	Electroplating	Silica, silicides, carbides, ash, plating bath constituents	F008
7.	Waste rinse water	Drag-out, equipment cleaning, spills	same as No. 1 and 2, but in lower concentrations	--
8.	Wastewater treatment sludge	Wastewater treatment	Metal hydroxides, sulfides, carbonates	F006
9.	Vent scrubber wastes	Vent scrubbing	similar to No. 7	--
10.	Ion exchange resin reagents	Demineralization of process water	brine, HCl, NaOH	--

Contaminated rinse water accounts for the large majority of waste produced on a volume basis. Rinse water is used to remove the drag-out from a workpiece after it is removed from a bath. Drag-out refers to the excess cleaning or plating solution that adheres to the workpiece surface, and gets carried out of the solution bath upon withdrawal of the workpiece from the bath. In general, the use of small part barrels in the plating process (barrel plating) produces more drag-out than rack plating. This is because a barrel carries with it more plating solution upon withdrawal from the bath than a rack does, and because drainage of the drag-out back into the bath is more difficult with barrels. If the drag-out from one bath is carried into the next bath in sequence due to incomplete rinsing, it is referred to as "drag-in", and is considered a contaminant in the later bath. Large amounts of rinse water are used on the workpiece at several points in a typical process, as shown in Figure 6-1.

Spent cleaning and plating solutions are another waste source. Several types of cleaning solutions are used to prepare a metal surface for electroplating. Stripping wastes are a special type of cleaning waste. They result from the stripping off of the old plated deposit prior to the deposition of a new metal plate. As shown in Table 7-1, cleaning solutions may be acidic or basic, and may contain organics. Heavy metals are usually not present, although some cleaning solutions contain cyanide. Spent plating solutions contain high concentrations of metals. These solutions are not regularly discarded like cleaning solutions, but may require purging if impurities build up.

Wastes produced from spills and leaks are usually present to some extent in an electroplating process. Water is used to wash away floor spills, and the resulting wastewater contains all of the contaminants present in the original solutions. Wastewater is also produced from the wet scrubbing of ventilation exhaust air.

The wastewater produced in the electroplating process may contain a variety of heavy metals and cyanide. The metals are removed by adding lime or other precipitating agents, and precipitating under alkaline pH. The resulting metal hydroxide precipitate forms a dilute sludge, which is thickened and then disposed of by landfilling. Figure 7-1 shows a typical electroplating wastewater treatment system.

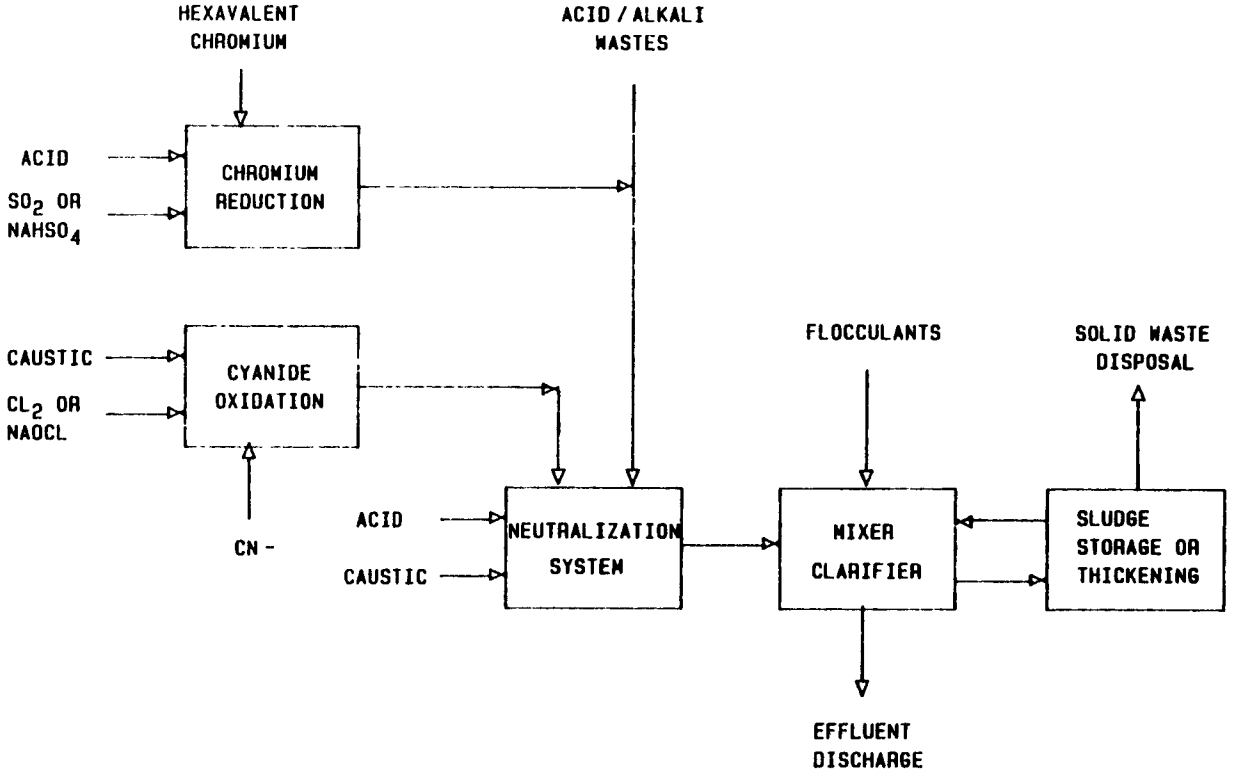


Figure 7-1 Wastewater Treatment System for Electroplating Wastes

8. WASTE GENERATION RATES

Very little data were available on overall waste generation rates from the electroplating industry. In 1976, Battelle Columbus Laboratories reported waste generation rates of metal hydroxides and degreaser sludges from the industry. Since these rates are 10 years old and narrow in scope (they do not account for current industry practices, nor do they cover all wastes generated), no annual volumetric rates could be obtained. Fractional waste generation rates (the percentage each waste represents of the total waste generated) were estimated by project staff, based on the available information and on industry comments. These values are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

The ten primary waste streams are presented in Table 7-1 along with their process origin. From a source reduction standpoint, these waste streams can be grouped as follows to reflect their common process origin:

- Work cleaning wastes
- Spent plating solutions and sludges
- Waste rinsewater
- Treatment wastes

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" have also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practices:

- o Waste stream segregation
- o Personnel practices
  - Management initiatives
  - Employee training
- o Procedural measures
  - Documentation
  - Material handling and storage

- Material tracking and inventory control
- Scheduling

o Loss prevention practices
  - Spill prevention
  - Preventive maintenance
  - Emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Work Cleaning Wastes (Nos. 1-4, Table 7-1)

Work cleaning wastes from electroplating processes are similar to the cleaning wastes produced in many other manufacturing processes. A detailed discussion of source reduction methods for cleaning wastes is provided in a separate practice study entitled "Metal Parts Cleaning", Section B20.

9.1.2 Spent Plating Solutions and Sludges (Nos. 5 and 6, Table 7-1)

Plating solutions such as those listed in Table 6-1 contain high concentrations of heavy metals, cyanides, and other toxic constituents. They are not discarded frequently, but rather are used for long periods of time. Nevertheless, they do require periodic replacement due to impurity build-up or the loss of solution contituents by drag-out. When a plating solution is contaminated or exhausted, the resulting waste solution is highly concentrated with toxic compounds and requires extensive treatment. The source control methods available for reduction of spent plating waste include:

o Increasing the longevity of the plating solution.
  The lifetime of a plating solution is limited by the accumulation of impurities and/or by depletion of constituents due to drag-out. The impurities come from five sources: racks, anodes, drag-in, water make-up, and air. The impurities buildup can be limited by the following techniques:

  - Purer anodes.
    During the plating process, metal from the anode is dissolved in the plating solution and deposited on the cathode (workpiece). Some of the impurities contained in the original anode matrix will stay behind

in the plating solution, eventually accumulating to prohibitive levels. Thus, the use of purer metal for the anode will extend the plating solution life.

- Drag-in reduction by better rinsing.
  Efficient rinsing of the workpiece between different plating baths reduces the drag-in of plating solution into the next bath.

- Use of deionized or distilled make-up water.
  To compensate for evaporation, water is required for makeup of plating solutions. Using deionized or distilled water is preferred over tap water, since tap water may have a high mineral or solids content, which can lead to impurity buildup.

- Plating solution regeneration through impurity removal.
  There are methods that have been successfully used to increase the longevity of plating solutions through impurity removal. More efficient filtering of a plating solution kept levels of impurities low and extended solution life (McRae 1985). In cyanide baths, carbonate tends to build up in solution over time due to CO_2 absorption from the air. This leads to solution deterioration. Reducing the carbonate concentration has been accomplished using a technique developed by the U.S. Army (U.S. Pat., 4,365,481), which involves freezing the carbonates out of solution. A metal box containing dry ice and acetone is immersed in the plating bath. Carbonates are precipitated directly onto the outside metal surface of the box, which is then removed from the solution. The carbonates are scraped off the box and discarded as solid waste, with a volume considerably smaller than that of the sludge associated with the spent plating solution.

- Proper rack design and maintenance.
  Corrosion and salt buildup deposits on the rack elements will contaminate plating solutions upon chipping and falling into the solution. Proper design and maintenance (cleaning) will minimize this form of contamination.

- Replacement of cyanide plating solutions with cyanide-free solutions
  A cyanide-zinc solution was replaced with a non-cyanide, non-chelated alkaline zinc solution (Olsen 1973, Lowenheim 1979). This eliminated the problem of handling cyanide-containing wastes. Other cyanide-free zinc solutions*, along with cyanide-free pyrophosphate copper plating solutions, have been used as replacements (Lowenheim 1979). Replacing cyanide solutions with non-cyanide solutions, however, often requires upgrading of the degreasing/cleaning techniques used. This is because the non-cyanide replacements may require a much more thoroughly cleaned surface to ensure high quality plating (USEPA 1981). The primary barrier to non-cyanide bath use is that military contracts often specify the use of cyanide solutions, thereby preventing electroplaters from using non-cyanide replacements**.

- Replacement of cadmium-based plating solutions with zinc solutions.
  The use of cadmium has been replaced with zinc in many applications*. See Section 10.1.1 for a detailed discussion of cadmium plating alternatives.

- Replacement of hexavalent chromium with trivalent chromium.
  Trivalent chromium, which can easily be precipitated from wastewater, has been used in place of toxic hexavalent chromium (Lowenheim 1979). However, trivalent chromium produces a lower quality surface, and has not seen widespread use.

- Return of spent plating solution to manufacturer.
  This option requires on-site segregation of solutions according to the metal in the solution. Only a few suppliers (Harshaw, CP Chemical) reprocess some spent bath solutions from their customers.

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* Alexandria Metal Finishers 1985: Personal communication.
** National Association of Metal Finishers 1985: Personal communication.

9.1.3 Waste Rinse Water (No. 7, Table 7-1)

Waste rinse waters account for the largest fraction of waste volume produced in electroplating processes. Any method of reducing the amount of rinse water used will significantly reduce the total waste volume from a process. Large amounts of rinse water are used to rinse off drag-out on a metal surface after the metal is removed from a plating or cleaning bath. Rinse waters usually contain dilute solutions of several toxic materials, such as cyanides and heavy metals. There are several methods available to reduce the amount of toxicity of waste rinse water produced. They can all be grouped into two major techniques: drag-out minimization and rinse water minimization. It must be pointed out that reducing drag-out will result in a decrease of the heavy metal content of the ultimate waste (treatment sludge), but the decrease in water consumption will affect only the volume of the co-precipitated calcium and magnesium hardness. Decreasing the amount of rinsewater without reduction in drag-out may thus result in the smaller, but more highly toxic, volume of treatment sludge.

9.1.3.1 Drag-out Minimization

By minimizing the amount of drag-out carried from a plating or cleaning bath to a rinsing bath, a smaller amount of water is needed to rinse off the workpiece. Also, less of the plating solution constituents leave the process, which ultimately produces savings in raw materials and treatment/disposal costs. The amount of drag-out depends on the following factors:

- Surface tension of the plating solution.
  A plating solution with a high surface tension tends to be retained in the crevices and surface imperfections of the workpiece when it is removed from the plating bath, thus increasing drag-out.

- Viscosity of the plating solution.
  Highly viscous solutions result in larger amounts of drag-out.

- Physical shape and surface area of the workpiece.
  The shape of the workpiece affects the amount of plating solution that gets dragged out of the bath. With all other parameters

remaining the same, a larger workpiece surface area results in more drag-out. It must be noted that barrel plating operations produce more drag-out than rack plating.

- Speed of workpiece withdrawal and drainage time.
  The rate at which the workpiece is withdrawn, the time allowed for drainage over the mother tank, as well as the orientation with which the work is withdrawn from the bath, affect the amount of drag-out produced.

Generally, drag-out minimization techniques include:

o Increasing plating solution temperature.
  The increased temperature lowers both the viscosity and surface tension of the solution, thus reducing drag-out. The resulting higher evaporation rate may also inhibit the carbon dioxide absorption rate, slowing down the carbonate formation in cyanide solutions. Unfortunately, this benefit may be lost due to the formation of carbonate by the breakdown of cyanide at elevated temperatures*. Additional disadvantages of this option would include higher energy costs, higher chance for contamination due to increased make-up requirement, and increased need for air pollution control due to the higher evaporation rate.

o Lowering the concentration of plating bath constituents.
  A decrease in the concentration of metal salts and other components of the plating solution leads to lower solution viscosity. This results in less dragout volume and lower metal losses. Additionally, lower concentration will also reduce the rinsing requirement. For example, it has been found that acceptable chromium plate can be obtained from baths containing only 25-50 g/l CrO_3 compared to traditional concentration of 250 g/l CrO_3 (USEPA 1981). The lower chromium concentration also results in a lower solution viscosity, which reduces drag-out.

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* National Association of Metal Finishers 1985: Personal communication

- Reducing the speed of withdrawal of workpiece from solution and allowing ample drainage time.

  The faster the workpiece is removed from the bath, the higher the drag-out will be. The workpiece should be removed as slowly and as smoothly as possible. Ample time should be allowed for draining the solution back to the tank, especially for higher viscosity solutions. Usually, 30 seconds allows most of the dragout to drain back to the tank. However, in applications where quick drying is a problem, a 10 second draining still permits good drag-out recovery*.

- Use of surfactants.

  Wetting agents have been used to lower the surface tension of plating solutions. A solution with a high surface tension is retained in the crevices and surface imperfections of the workpiece upon removal from the plating bath. By reducing the surface tension, drag-out is greatly reduced. Applied in only small amounts, wetting agents can lower a solution surface tension enough to reduce drag-out by up to 50% (USEPA 1981). Only non-ionic wetting agents, which will not be degraded by electrolysis in the plating bath, should be used. The use of surfactants is sometimes limited due to their adverse effect on the quality of the plate produced**.

- Proper positioning of the workpiece on the plating rack.

  When a workpiece is lifted out of a plating solution on a rack, some of the excess solution on its surface (drag-out) will drop back into the bath. Proper positioning of the workpiece on a rack will facilitate the dripping of the drag-out back into the bath. The position of any object which will minimize the carry-over of drag-out is best determined experimentally, although the following guidelines were found to be effective (USEPA 1981):

  - Orient the surface as close to vertical as possible.
  - Rack with the longer dimension of the workpiece horizontal.
  - Rack with the lower edge tilted from the horizontal so that the runoff is from a corner rather than an entire edge.

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* Westinghouse Electric Corporation 1985: Personal communication.

**National Association of Metal Finishers.

By redesigning racks for better drainage and reducing the metal concentration in the plating bath, drag-out was reduced at one plant by 55%. This, in turn, greatly decreased rinse water requirements (Anonymous 1985a).

- Improved drag-out recovery.
  A drain board positioned between a plating bath and rinse bath can capture the dripping solution off of a workpiece and route it back to the plating bath. This is a simple operation which has been incorporated into many electroplating processes. The drain board can be made of either plastic or metal. For acidic solutions, it has been suggested that drain boards be made of vinyl chloride, polypropylene, polyethylene, or Teflon*-lined steel (USEPA 1981). Another commonly practiced option is to incorporate a drip tank between the plating bath and the rinsing bath. The drip tank is an empty tank for collecting the dripping solution, which can be returned to the plating bath.

9.1.3.2 Rinse Water Minimization

Another method of waste rinse water reduction is to rinse off the workpiece in the most efficient manner, using the smallest volume of rinse water. Traditionally, a workpiece would be immersed into a single rinsing bath following a plating bath, and then moved on to the next step in the process. Several methods exist which use less rinse water than the traditional rinsing method, while still adequately rinsing the workpiece. These include:

- Multiple rinsing tanks.
  The use of multiple rinsing tanks is one of the most commonly used source reduction techniques. Virtually all new electroplating plants are designed with multiple rinsing tanks, which can reduce rinse water requirements by 66%**, with possible theoretical reductions of over 90% reported (USEPA 1983, USEPA 1981, Olsen 1973). Multiple rinsing tanks are aligned either in series or in parallel. In a three-tank rinsing system, a workpiece is moved from a plating solution to the first rinse tank, then onto the second rinse tank, then to the third, and finally onto the next step in the process.

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* National Association of Metal Finishers 1985: Personal communication.
** Registered trademark of E. I. Du Pont.

In the parallel arrangement, each rinsing tank is individually fed with fresh rinsing water. The more common series arrangement differs in that it is a counterflow system. In a three tank counter-current system, the workpiece enters the first rinse tank, which has the most contaminated rinse water. It is then moved to the second tank, and then to the last, where it contacts fresh rinse water. Fresh rinsewater enters only the last (third) rinsing tank. The water from the third tank then flows into the second tank, then into the first tank from which it can be routed into treatment and/or to the plating tank as a make-up.

- Fog nozzles and sprays.

  Spraying water droplets directly onto a workpiece is much more efficient than immersing a workpiece into a liquid water bath. The only limitation is that spraying is not effective on oddly-shaped objects, since the spray cannot make direct contact with the entire surface of the object. For simple workpieces, such as sheets, it is highly effective.

  A variation on the spray nozzle is the fog nozzle. A fog nozzle uses water and air pressure to produce a fine mist. Much less water is used than with a conventional spray nozzle. It is possible to use a fog nozzle directly over a heated plating bath to rinse the workpiece. This allows for simultaneous rinsing and replenishment of the evaporated losses from the tank. Spray or fog rinsing is used on rack plating, which represents a third of all plating operations. Nozzles are not applicable for barrel plating (two thirds of all plating operations) because of the odd shape of the parts *.

- Rinse water reuse.

  By using the same rinse water stream at more than one step in the process, the total amount of waste rinse water produced is drastically reduced. After a rinse water is used once, it picks up contaminants from the workpiece that was rinsed. If these contaminants do not interfere with the quality of a subsequent plating step, the same water can be used again. For example, in a nickel plating process, the same rinse water stream

* Baxter and Wardman Eng. 1985: Personal communication.

was used for the rinses following the alkaline cleaning, acid dip, and nickel plating tanks. Instead of having three different rinse streams, only one stream was used, greatly reducing the overall rinse water requirements (USEPA 1983).

- o Still rinsing.
  Installing a still (or dead) rinsing tank immediately after a plating bath allows for metal recovery and lowered rinse water requirements. In such a system, the workpiece is immersed in a still rinse tank following the plating bath. Since the still rinse has no inflow or outflow of water, the concentrations of the plating bath constituents build up in it. When the concentration becomes sufficiently high, the contents of the still bath are used to replenish the upstream plating bath.

- o Automatic flow controls.
  The lowest possible rinse water flow rate which can efficiently rinse a workpiece can be determined for all systems. This flow then can be automatically controlled to avoid variations associated with water line pressure changes and manual control by operator.

- o Rinse bath agitation.
  Agitating a rinsing bath mechanically or with air increases the rinsing efficiency and cuts down on water demand.

9.1.4 Treatment Wastes (Nos. 8-10, Table 7-1)

In electroplating, toxic metal sludges result from the conventional treatment processes used to remove metals from aqueous wastes. Metals are usually precipitated as hydroxides or carbonates, resulting in a sludge which requires further treatment and disposal. Lime is commonly used as the precipitating agent. The volume and toxicity of the sludge produced can be lowered by reducing the metal content in the plating and rinse waste waters, or by using different precipitating agents. Methods available to accomplish this include:

- o Use of different precipitating agents.
  Normally, hexavalent chromium in waste rinse water or plating solutions is treated by being reduced to trivalent chromium with a reducing agent,

followed by precipitation with lime. In one instance, sodium hydroxide was used in place of lime (Chacey 1983). Lime precipitation produced 2.24 dry solids/lb Cr (VI), while sodium hydroxide precipitation produced only 1.98 lb dry solids/lb Cr (VI).

- Use of trivalent chromium instead of hexavalent chromium for plating.
  One operation reported a 70% reduction in sludge production when trivalent chromium was used for plating instead of hexavalent chromium because of avoided necessity to precipitate gypsum associated with the excess sulfate ions that would have been introduced during reduction step. (Anonymous 1985a).

- More efficient sludge dewatering.
  The volume of sludge produced can be greatly reduced through the use of new dewatering technologies which remove a greater percentage of water than traditional dewatering techniques (Anonymous 1985b).

- Better operating practices (stream segregation).
  The type of waste requiring treatment can be controlled to some extent through waste stream segregation. By isolating cyanide-containing waste streams from waste streams containing iron or complexing agents, the formation of cyanide-complexes is avoided, and treatment made much easier (Dowd 1985). Segregation of wastewater streams containing different metals also allows for metals recovery or reuse. For example, by treating nickel-plating wastewater separately from other waste streams, a nickel hydroxide sludge is produced which can be reused to produce fresh nickel plating solutions. In one instance, the scrubber waste from a chromium plating bath was segregated and could then be returned to the bath. This resulted in less discarded waste and increased the longevity of the plating solution.

- Metal recovery techniques.
  Decreasing the heavy metal content of wastewater can be accomplished through drag-out minimization and also through recovery of these metals prior to treatment. By recovering the metals from the rinse waters, the toxicity and volume of the treatment sludge will be reduced, if not

eliminated. In addition, better raw material utilization will help to offset higher operating costs. The metal recovery techniques examined include:

- Evaporation
- Reverse osmosis
- Ion exchange
- Electrolytic metal recovery
- Electrodialysis
- Use of separate treatments for individual solutions

Evaporation - Waste rinse water is evaporated by heating, leaving behind a concentrated solution. The equipment used includes single or multiple effect evaporators. Also, vapor recompression applications were reported (Seaburg and Bacchetti 1982). The solution is concentrated until its metal concentration is equal to that of the plating bath, then this solution is reused. Using this method, 90-99% efficient metal recoveries can be achieved (Clark 1984). Depending on the design, the evaporated water vapor can either be condensed and re-used as rinse water, or it can be vented off into the atmosphere (Campbell and Glenn 1982). Evaporation has been used frequently for chromium recovery. One plant was able to recover 8,000 lbs of chromium per month, resulting in savings of $100,000/yr, with a one-year return on investment (Campbell and Glenn 1982). It has also been proven effective for the recovery of gold, nickel, copper, and cadmium (Kohl and Triplett 1984). Evaporation is best established of all the metal recovery techniques used in electroplating. Although it is the most energy intensive recovery technique, its simplicity and reliability make it an attractive option for metal recovery. In order for evaporation to be economical, multiple counter-current rinse tanks or spray/fog rinsing should be used to minimize the amount of rinse water being processed (MDEM 1984).

Apart from the energy cost, a distinct disadvantage is that the concentrates may also contain the calcium and magnesium salts originally present in the rinsewater. Adding them to the plating solution may result in more rapid deterioration. This problem is alleviated in situations where rinsewater is de-ionized or softened prior to use.

Reverse Osmosis - In reverse osmosis, a semi-permeable membrane is used to concentrate a dilute waste rinse water stream. The dilute waste is applied with high pressure to a membrane which allows the water to pass through, but retains the metals and other solutes present. Thus, on one side of the membrane, a concentrated metal solution is produced which can be returned to the plating bath; on the other side of the membrane, pure water is obtained which can be reused as rinse water.

Reverse osmosis has been used most successfully for nickel recovery, although it is also used to recover copper, zinc, and cadmium (Campbell and Glenn 1982, Kohl and Triplett 1984). It has not been extensively used for chromium recovery (Campbell and Glenn 1982). Reverse osmosis is less energy intensive than evaporation, but the characteristics of the membranes available limits the type of waste streams that can be treated. For example, only very dilute streams can be treated, and the solution must be pre-filtered to extend membrane life (MDEM 1984).

Ion Exchange - Ion exchange involves exchanging one ion from a solution with another ion in order to recover certain ions (such as metal ions) or to purify the solution. This occurs by passing a solution over an ion exchange resin which has the capacity of exchanging one of its own ions for an ion in solution. Once a resin has reached its capacity in terms of ions exchanged, it must be regenerated. Regeneration is usually accomplished using an acid or a base, depending on the type of resin. The acid or base removes the accumulated metal from the resin. Another step may be necessary to remove the metal from the acid or base before the metal can be reused. Ion exchange is often used for purification of rinse water, rather than simple metal recovery. Ion exchange has been effective for recovery of nickel, chromium, cyanide, gold, silver, and other metals (Kohl and Triplett 1984).

Ion exchange is a relatively complicated and delicate process which demands a high level of process control and maintenance. For this reason, as well as for other technical reasons such as regeneration problems, ion exchange is not currently a popular method for metal recovery.

Electrolytic Metal Recovery - In electrolytic metal recovery, metal ions in solution are reduced electrochemically onto a cathode surface within the solution. When the cathode becomes fully coated with the metal, it is removed from the solution and placed into a plating bath as an anode, replenishing the bath with the metal. Up to 99% of the metal in waste rinse water can be recovered using this method (Campbell and Glenn 1982). One great advantage of the electrolytic method over other metal recovery techniques is that it recovers only the plating metal, not the impurities, from the waste rinse water. Electrolytic metal recovery is most efficient on concentrated solutions. For solutions with less than 100 mg/l of the metal ion, low current efficiencies limit the process effectiveness. Electrolytic recovery systems have been used to recover copper, tin, gold, silver, cadmium, and other metals (Campbell and Glenn 1982, Kohl and Triplett 1984). In one application, the metal was recovered directly from a cyanide - destruct tank*.

Electrodialysis - In electrodialysis, an electric current and selective membranes are employed to separate the positive and negative ions from a solution into two streams. This is accomplished by feeding a solution through a series of alternating cation and anion selective membranes, through which a current is passed. Electrodialysis is used mainly to concentrate dilute solutions of salts or metal ions. Electrodialysis has been used to remove nickel, copper, cyanide, chromium, iron and zinc from waste rinse water (MDEM 1984, Kohl and Triplett 1984). This technology has not been used as widely in the electroplating industry as have other metal recovery techniques (Campbell and Glenn 1982, Kohl and Triplett 1984).

Use of Separate Treatments - Use of separate treatments for individual solutions results in a sludge that bears a single metal. The sludge (metal hydroxide) can then be sold, e.g., to a chemical producer.

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* National Association of Metal Finishers 1985: Personal communication.

9.2 Implementation Profile

The use of multiple rinse tanks, often with counterflow arrangements, is currently one of the most effective and widely used methods of waste reduction available. Most large plating operations, in fact, are built with multiple rinse tanks. Smaller shops, however, often use only a single rinse following immersion in cleaning and plating solutions.

The installation of a second and/or third rinse tank following a plating bath drastically reduces rinse water consumption, as discussed earlier. It also involves substantial process modifications. Since all of the baths and mechanical equipment in most electroplating shops are built in a series type of arrangement, the inclusion of additional tanks may require some changes in the shop lay-out. Besides the tanks themselves, piping, pumps, flow controllers, and racks for transporting the workpieces will need to be added. In some instances, the availability of space may be the determining factor in the use of multiple rinse tanks.

In smaller electroplating shops, rinsewater tanks may be over-sized for their specific applications. Instead of installing a second tank, it is often possible to simply divide the existing tank in half by constructing a wall (Dowd 1985). This effectively converts the single large tank into two smaller tanks. The additional piping needed is minimal.

A second waste reduction method with a high implementation potential is the reuse of rinse water. Electroplating operations use rinse water at several stages in the process, and it is often possible to use the same stream at more than one step.

Adding rinsing steps to an existing operation would necessitate modification of the piping system. The main technical problem with this technique is that the quality of the product must be monitored carefully. A rinse stream can be used a second time only if the contaminants from the first rinse do not interfere with the quality of the second rinse. Monitoring the rinse water composition and the quality of the workpiece after each rinse might be required.

As hazardous waste treatment and disposal costs rise, there is an incentive to implement waste reduction methods for the purpose of achieving cost reductions. Some of the waste reduction techniques discussed here involve minimal capital outlays. Examples of these would be good operating practices and rinse water reuse, which often entail minor equipment changes and/or simple changes in procedure. Smaller shops (roughly two-thirds of the industry) may find these methods practicable, but may be capital-constrained in the implementation of more extensive modifications. It has been shown that the use of multiple rinse tanks and other rinse water conservation methods, which vary considerably from one to the other in expense, can reduce waste treatment costs by $10,000 -$99,000 per year (David 1985).

9.3 Summary

The waste sources and their respective source control technologies are summarized in Table 9-1. The ratings listed in this table are based on a scale of 0-4.0 and are used to evaluate each technique for its waste reduction effectiveness, extent of current use, and further application potential. The ratings shown are based on a review of the available literature, as well as the opinions of industry personnel.

The most effective waste reduction methods include the use of multiple rinse tanks, the installation of drain boards and drip tanks, the reuse of rinse water, and the installation of metal recovery systems. Since waste rinse water accounts for the majority of the volume of waste produced, the methods which decrease rinse water consumption offer the greatest potential for waste reduction.

Based on the measures currently undertaken to reduce waste, a current reduction index of 1.8 (45 percent) has already been achieved by the electroplating industry. By implementing additional waste reduction methods or increasing the use of existing measures, the current quantity of waste produced could be reduced to the level corresponding to a future reduction index of 0.8 to 1.9 (20 to 48 percent). The above values mean that currently employed measures have reduced waste generation by 45 percent from the levels that otherwise would exist, and that future measures could reduce wastes by 20 to 48 percent from the current waste generation levels.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE ELECTROPLATING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Cleaning Solutions (*)	1 See study on Metal Parts Cleaning	---	---	---	---	---		2.0	1 2	1 9
	Overall	---	---	---	---	---	0 10	2 0	1 2	1.9
Spent Plating Solutions and Sludges (*)	1. Increase plating solution life	1	1	1	1	2		0.1	0 4	
	2 Use non-cyanide plating solutions	1	2	2	1	2		0 1	0 8	0.8
	3. Replace cadmium plating with zinc	1	2	2	1	2		0 1	0 8	0 8
	4 Replace hexavalent chromium with tri	1	2	3	1	1		0.2	0 6	
	Overall	1 00	1 75	2.00	1.00	1.75	0 15	0.2	0 6	0 8
Waste Rinse Water	1. Increase solution temperature	1	2	1	2	1		0.5	0.1	
	2 Use less concentrated plating soln	1	2	3	1	2		0.8	1 1	
	3. Withdraw workpiece slowly from soln.	2	2	2	1	3		0.5	1 1	
	4 Add wetting agents to plating soln.	2	1	1	1	2		0.3	0 4	
	5 Position workpiece properly on rack	3	3	2	3	2		1.5	0 3	
	6 Recover drag-out of plating solutions	2	1	2	2	3		1.0	0 8	
	7 Install multiple rinse tanks	3	3	4	2	2		2 0	1 0	
	8 Install fog nozzles and sprays	2	2	3	2	3		1 5	1 1	
	9 Reuse rinse water elsewhere in plant	1	2	4	1	3		1 0	2 3	2 3
	10. Install still rinsing tanks	1	1	2	2	3		1 0	0 8	
	11. Install automatic flow controls	2	1	3	2	2		1 5	0 8	
	12. Use mechanical/air agitation of bath	1	1	1	2	1		0.5	0 1	
	Overall	1 75	1.75	2.33	1.75	2 25	0 65	2 0	0 8	2 3
Treatment Wastes (*)	1. Use efficient precipitating agents	1	2	2	1	2		0.5	0 8	
	2 Use trivalent instead of hex chromium	1	2	3	1	1		0.8	0 6	
	3. Install sludge dewatering systems	1	2	4	1	1		1 0	0 8	
	4. Implement better operating practices	1	2	3	1	2		0.8	1.1	
	5. Install metal recovery systems	3	3	3	1	3		0.8	1 7	1 7
	Overall	1.40	2 20	3 00	1 00	1 80	0 10	1.0	1 0	1 7
All Sources	All Methods						1 00	1.8	0.8	1 9

(*) These waste streams include listed "F" and/or "K" RCRA wastes

10. WASTE REDUCTION THROUGH PRODUCT SUBSTITUTION

This study has so far examined methods of reducing the amount of waste produced in electroplating operations through process modifications or other changes. It is also possible to reduce or eliminate the generation of certain wastes through product substitution. A complete investigation of product substitutions has not been attempted; rather, two possible product substitutions are briefly discussed below.

10.1 Cadmium Plating Alternatives

Cadmium is used in a wide variety of products for its excellent protective properties. Cadmium-plated products are highly resistant to corrosion in land and marine environments. For this reason, the U.S. military specifies cadmium plating for a large variety of naval and aerospace equipment*. Roughly 35-40% of the total amount of cadmium consumed in the country is used by the U.S. military**. Unfortunately, cadmium is extremely toxic and there is concern over the introduction of soluble cadmium salts into the environment.

It may be possible in some instances to replace cadmium plating with other materials such as:

- o Zinc using plating (zinc graphite has been considered an alternative to cadmium).
- o Titanium dioxide using vapor deposition.
- o Aluminum using ion vapor deposition (Ivodizing).

None of the above-mentioned coatings have exactly the same properties as cadmium, but nonetheless may prove to be satisfactory substitutes. Aluminum ion vapor deposition is a very attractive process, but is considerably more expensive than electroplating*.

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* Cadmium Council 1985: Personal communication.
** National Association of Metal Finishers 1985: Personal communication.

The elimination of cadmium from industrial use has already been attempted. In 1979, Sweden began the first stage of a ban on the use of cadmium in electroplating and in various pigments. It was hoped that this would lower the concentration of cadmium found in the environment over time. The ban has not achieved this end, and Sweden is considering removing the current regulations on the use of cadmium*.

The elimination of the use of cadmium is not being endorsed by the electroplating industry. The implementation of such a change would require major modifications to many electroplating shops, and could result in the closing down of some shops altogether.

10.1.2 Chromium Plating Alternatives

Chromium is used to plate a multitude of products ranging from automobile parts to paper clips. In some instances, the chromium plate is required for its hardness and durability. In other cases, it is used purely for decorative reasons.

Because there is a substantial amount of waste produced during a chromium plating operation, the elimination of any unnecessary use of chromium would be beneficial from the environmental standpoint. For example, chromium-plated automobile bumpers could be replaced with nickel-plated bumpers, although customer preference for a shinier finish may play a major role. Of course, the substitute product must have less waste associated with its production than does the original product. Many automobile bumpers are currently being painted rather than plated during finishing operations*.

As with cadmium, industry does not seem to be promoting the elimination of chromium use on certain products. The economic reasons that could justify such a change today are not present. Since the majority of electroplating operations are small and employ less than 20 people, (Dun's 1982, USDC 1985) the capital needed to implement major process changes is often not available.

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* General Motors Corp., 1985: Personal communication.

11. CONCLUSIONS

To reduce the problems of waste treatment and disposal in the electroplating industry, many methods of waste reduction through source control have been identified. It is estimated that the total waste output from electroplating can be further reduced by 20 to 48% by implementing or expanding the use of the source reduction methods discussed. The most efficient methods available for waste reduction are using multiple rinse tanks, installing drain boards and drip tanks, and reusing rinse water. The electroplating industry already appears to have implemented waste reduction measures to a fairly high degree, as evidenced by the current waste reduction index value of 1.8 (45 percent).

The technology associated with the waste reduction methods discussed is readily available and well understood. Economic constraints have been the major barrier to implementation.

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1. PROCESS: EPICHLOROHYDRIN MANUFACTURE

2. SIC CODE: 2869

3. INDUSTRY DESCRIPTION

The epichlorohydrin manufacturing industry comprises firms engaged in both the production and use of epichlorohydrin. The establishments are part of large multiproduct corporations.

3.1 Company Size Distribution

In the U.S., crude and refined epichlorohydrin is currently produced at three locations by only two companies. The total U.S. production capacity of the epichlorohydrin industry in 1982 was 290,000 short tons. An epichlorohydrin facility employs approximately 50-60 persons; the work force includes production workers (operators), supervisory personnel, and maintenance personnel (Bales 1978).

3.2 Principal Producers

There are two major producers of epichlorohydrin in the United States:

Dow Chemical Company
Shell Chemical Company

3.3 Geographical Distribution

Of the three epichlorohydrin manufacturing facilities in the United States, two are in Texas, and one is in Louisiana. All are located in EPA region VI. See Table 3-1 for a listing of company locations.

Table 3-1 Epichlorohydrin Producers in the United States

Company	Production tons/year	Capacity tons/year	Percent of Total
Dow Chemical USA Freeport, Texas	123,000	210,000	72
Shell Chemical Co.			
Deerpark, Texas	33,500	80,000	28
Norco, LA	33,500	incl.	incl.
Total	190,000	290,000	100.0

Source: Chemical Economics Handbook (SRI 1982) and industry comments.

4. PRODUCTS AND THEIR USE

Based on 1982 statistics, approximately 19% of the crude epichlorohydrin produced in the U.S. was used to make synthetic glycerin. Glycerin is used in the making of alkyd resins, explosives, polyether polyols, cosmetics and drugs, cellophane, food and beverages, and in other miscellaneous applications. Approximately 62% of the epichlorohydrin (after further refining) was used in the making of unmodified epoxy resins. These resins are used for making protective coatings, reinforced plastics, and adhesives. About 2.3% of the refined epichlorohydrin was used to make epichlorohydrin elastomers. The remaining 14% was used for making a variety of other miscellaneous products including glycidyl ethers, some types of modified epoxy resins, wet strength resins for the paper industry, water treatment resins, surfactants, and ion exchange resins. Table 4-1 presents a breakdown of epichlorohydrin uses.

Table 4-1 1982 Epichlorohydrin Products and Use Distribution

Epichlorohydrin Use	Breakdown Percent
Glycerin	18.6
Unmodified epoxy resins	62.0
Epichlorohydrin elastomers	2.3
Miscellaneous	14.1
Total	97.0(a)

Source: Chemical Economics Handbook (SRI 1982).
a) Some epichlorohydrin is lost during the refining process.

5. RAW MATERIALS

The raw materials used to produce epichlorohydrin are shown in Table 5-1. Both Dow and Shell Chemical make epichlorohydrin from an allyl chloride intermediate synthesized from propylene and chlorine.

Table 5-1 Raw Materials Used by the Epichlorohydrin Manufacturing Industry

Raw Materials	Usage lb/lb product
Propylene	Not Found
Chlorine	Not Found
Allyl Chloride	.997
Chlorine	.9025
Slaked Lime	1.009

Source: Assessment of Hazardous Waste Practices (Gruber 1975).

6. PROCESS DESCRIPTION

Currently, both producers of epichlorohydrin use a process involving the use of allyl chloride as an intermediate reactant. Simplified process flow diagrams are depicted in Figures 6-1 and 6-2. The first step is the production of allyl chloride from propylene and chlorine:

$$H_2C = CHCH_3 + Cl_2 \text{ ---- } H_2C = CHCH_2Cl + HCl$$

The byproducts include 1,2-dichloropropane and isomers of 1,3-dichloropropene.

The second step is chlorohydroxylation of allyl chloride to dichlorohydrin (C_3H_6OCl):

$$ClCH_2 - CH = CH_2 + HOCl \text{ ----} \begin{matrix} Cl\,CH_2\text{-}CH(OH) - CH_2Cl & 1,3 \text{ - dichlorohydrin} \\ ClCH_2 - CHCl - CH_2OH & 1,2 \text{ - dichlorohydrin} \end{matrix}$$

The byproduct formed in this reaction is 1,2,3 - trichloropropane.

The third reaction step is the conversion of dichlorohydrin to epichlorohydrin:

$$2\,C_3\,H_6\,O\,CL_2 + Ca(OH)_2 \text{ ----} \rightarrow 2ClCH_2 - \underset{\backslash\,O\,/}{CH} - CH_2 + CaCl_2 + 2H_2O$$

(or 2NaOH; or 2NaCl)

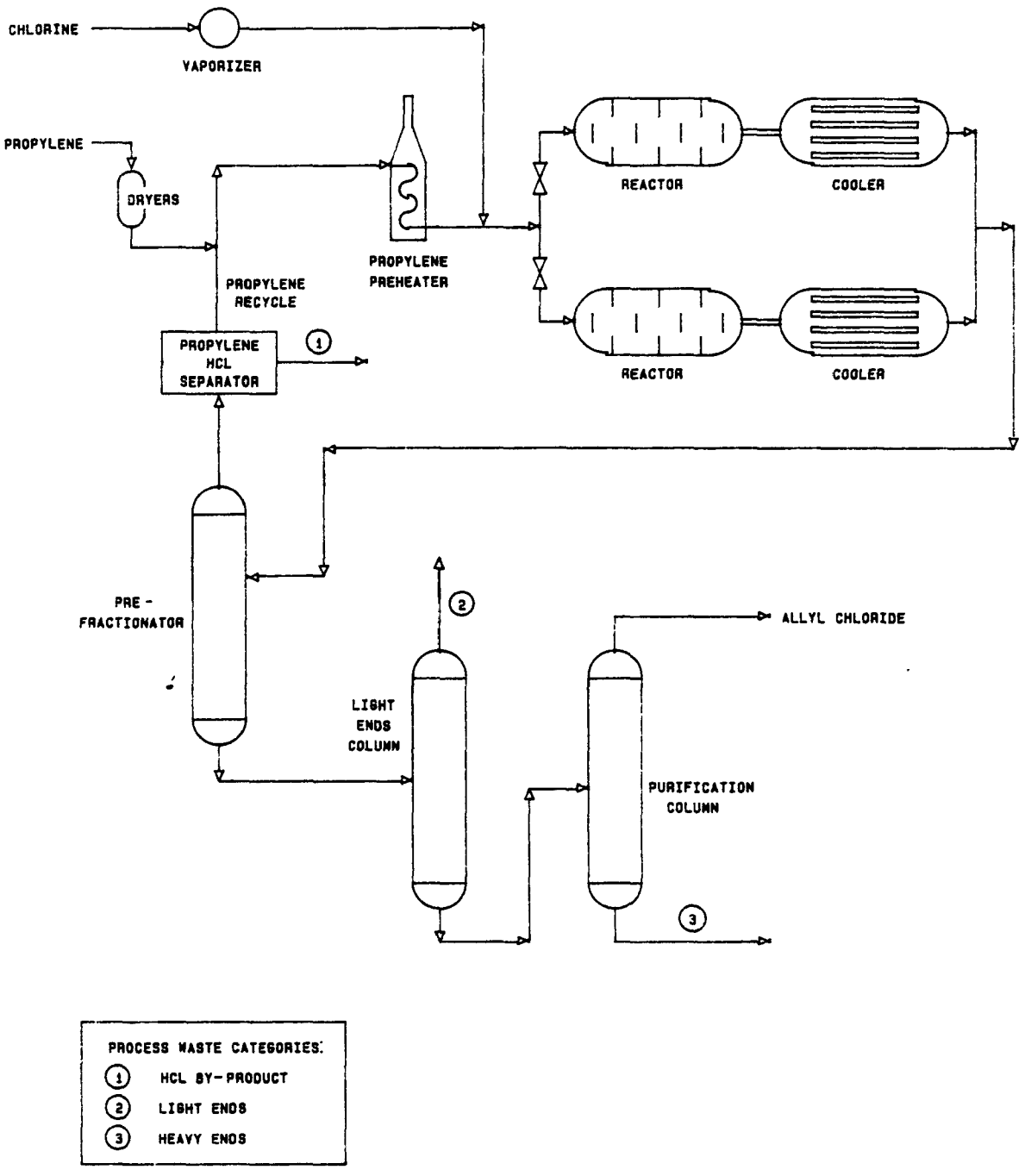

Figure 6-1 Allyl Chloride Synthesis from Propylene and Chlorine

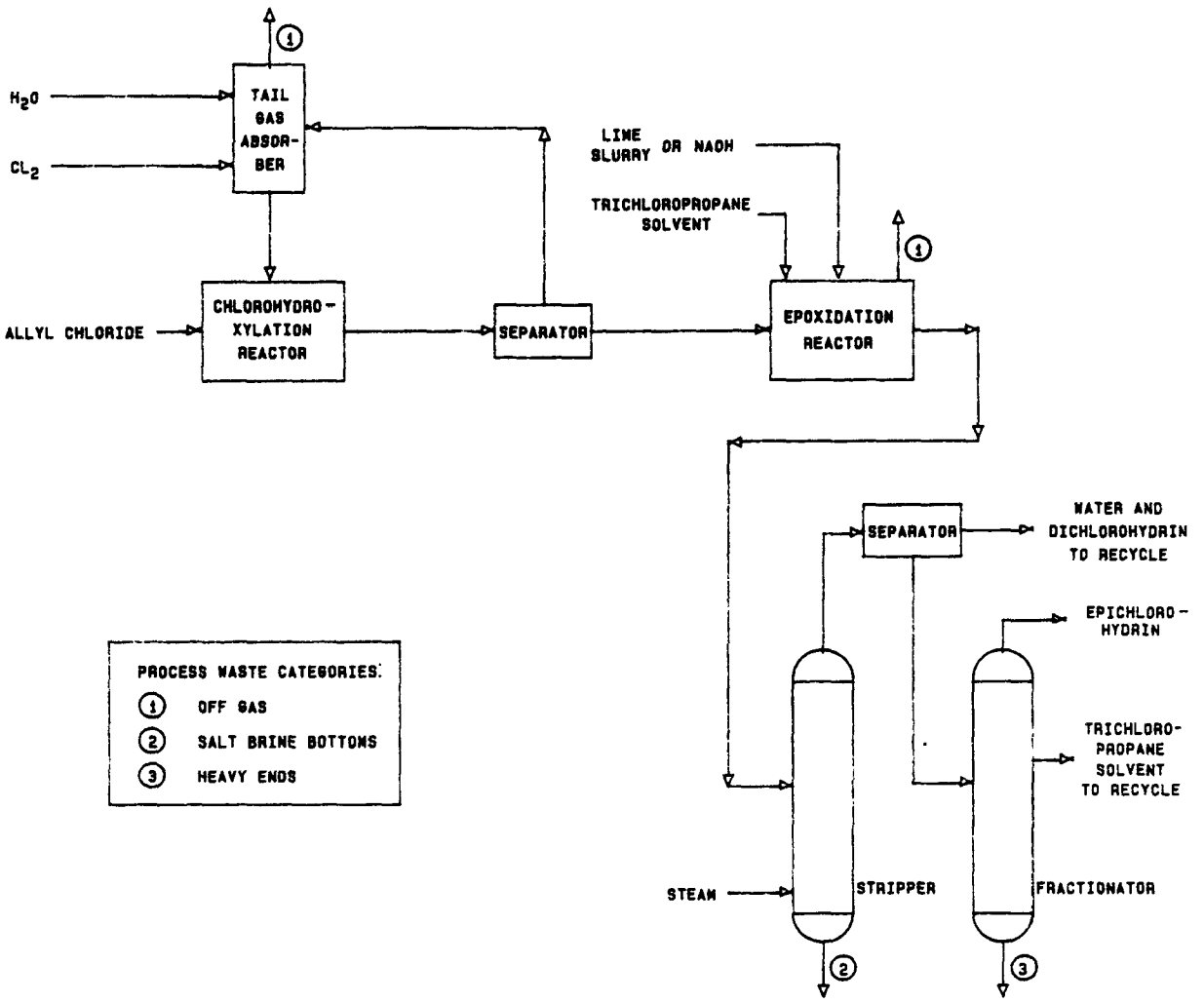

Figure 6-2 Epichlorohydrin Production from Allyl Chloride

In the first step, excess propylene and chlorine gas are continuously fed into an adiabatic non-catalytic reactor at 930-950°F and 30 psia to produce allyl chloride and HCl. The reactor effluent is cooled to about 120°F and sent to a pre-fractionator to separate HCl and propylene. The overhead stream gas stream is subsequently split at cryogenic conditions; propylene is recycled to the propylene preheater and HCl is taken off for other uses in the integrated halogenated hydrocarbon facility.

After initial removal of HCl and propylene, the organic chloride fraction is separated in a two-step distillation. Low boiling constituents are taken overhead in the first column. These include various saturated chlorides such as 2-dichloropropane. The heavy-boiling fraction which is taken off as a bottom product in the second column, is made up largely of unsaturated dichlorides and other allyl chloride degradation products such as benzene, tars, and carbon (DeBenedictis 1979). This fraction, rich in 1,3 - dichloropropene, is used as a feedstock to the process of manufacturing fumigants or nematicide formulations, such as D-D (Shell Chemical Co.) or Telone II (Dow Chemical)

The allyl chloride overhead stream from the second column is fed continuously to a stirred tank where it reacts in the liquid phase (at atmospheric pressure and 85-105°F) with a solution of hypochlorous acid. The hypochlorous acid is produced in a packed tower by dissolving chlorine in water. The reaction tank effluent is fed to a gravity separator: the upper layer (aqueous phase) is recycled to the hypochlorous acid tower. The underflow, chiefly dichlorohydrins, is fed to the second reactor, where virtually complete conversion to epichlorohydrin by reaction with aqueous NaOH or lime takes place. Trichloropropane, one of the reaction co-products is used as a solvent for the epichlorohydrin. The effluent from the second reactor is steam stripped, removing epichlorohydrin as the water azeotrope. The undercut (calcium chloride or sodium chloride solution and excess lime in suspension) is sent to by-product recovery. The distillates, water, and organic phases are separated, with the undercut fed to a fractionating tower for recovery of epichlorohydrin and solvent. The epichlorohydrin is purified and sent to storage. The recovered trichloropropane solvent is recycled to the product reactor. Some process configurations, however, do not incorporate this recycle stream.

The small amount of dichlorohydrins carried over from the steam stripper in the epichlorohydrin-water azeotrope is mostly discharged in the water phase from the second separator. This aqueous dichlorohydrin is recycled. The heavy ends, discharged as still bottoms from the fractionator, contain some epichlorohydrin, 5 percent dichlorohydrin, 7 percent chloroethers, 35 percent trichloropropane, and 50 percent heavies or tars (Gruber 1975).

7. WASTE DESCRIPTION

The wastes evolved in the epichlorohydrin manufacturing process come primarily from the off-streams or bottom streams of the various recovery steps. The specific RCRA codes and waste stream compositions are given in Table 7-1. Most of the by-products from the process have found application as feedstocks to other processes. For example, light ends from the allyl chloride synthesis step are oxidized to recover HCl and heat of combustion. Therefore, the label "waste stream" would not apply to those facilities which reprocess the light ends in the above fashion. Sections below give descriptions of treatment and disposal practices found in the literature or through contacts with the industry*.

- HCl Byproduct from Allyl Chloride Synthesis.
  In an integrated chlorohydrocarbon facility, HCl is recovered, e.g., by routing it to the oxychlorination unit associated with the vinyl chloride monomer production.

- Light Ends
  The light ends from the allyl chloride synthesis step are oxidized to recover HCl and heat.

- Heavy Ends
  The heavy ends from the allyl chloride purification column contain 1,3 - dichloropropylene, an active ingredient of fumigant or nematicide formulations. Hence, this stream is often used as a feedstock to a process to manufacture such formulations. The remainder is either landfilled or oxidized for HCl or heat recovery. The heavy ends from the

* Dow Chemical Co. 1985: Personal communication

Table 7-1 Epichlorohydrin Process Effluent Streams

No.	Waste/Residual	Process Origin	Composition[a] (lb/lb epichlorohydrin)		RCRA Codes
1.	HCl By-Product	HCl Separator	HCl (1 lb/lb allyl chloride)		--
2.	Light Ends	Light Ends Column	N/A		--
3.	Heavy Ends	Allyl Chloride Purification Column	N/A		--
		Epichlorohydrin Fractionator	Heavy Ends	.053	K017
			Chloroethers	.0074	
			Epichlorohydrin	.001	
			Dichlorohydrin	.0057	
			Trichloropropane	.037	
4.	AC Reactor Tars	Allyl Chloride Reactor	N/A		F024
5.	Off Gas	Tail Gas Absorber	Allyl Chloride	.002	--
			Chlorine	Trace	
			HCl	Trace	
		Epoxidation Reactor	Allyl Chloride	.002	--
			Epichlorohydrin	.0015	
			Trichloropropane	.0005	
			Chlorine	Trace	
			HCl	Trace	
6.	Salt Brine Bottoms	Salt Stripper	$CaCl_2$ or NaCl	.600	--
7.	Equipment Cleaning Sludge	Cleaning of Columns, Tanks and Heat Exchangers	N/A		F024
8.	Spills and Leaks		N/A		--

(a) Source: Assessment of Industrial Hazardous Waste Practices (Gruber 1975) for composition data.

epichlorohydrin fractionator are either landfilled, burned to recover HCl or energy or used as feedstock to other processes. They contain high concentrations of 1,2,3-trichloropropane, a byproduct of chlorohydroxylation reaction.

- Salt Brines
  Salt brines from the epichlorohydrin stripper leave the process via bio-oxidation treatment units to remove organics. The water solution of salts ($CaCl_2$ or NaCl) is not considered hazardous.

- Miscellaneous Process Equipment Cleaning Wastes
  The cleanup sludges from heat exchanger tube cleaning and steamout oils from columns or tanks are generated infrequently, (at 1 to 2 year intervals). The main waste stream in this category is generated by cleaning of the allyl chloride reactor, which occurs presently every 2 months*. The current disposal practice at all sites is not known, although one facility reported that these wastes are recycled to the process.

- Spills and leaks
  Because of the toxicity of epichlorohydrin and its process intermediates, the potential leak sources, such as valve packings, pump seals, and flange gaskets are routinely inspected and maintained. Consequently, leakage is minimal (Bales 1978).

Epichlorohydrin is shipped in drums, tank cars, or via pipeline. Epichlorohydrin is pumped directly from storage tanks and introduced into the drums through a retractable pipe with a cut off valve immediately above the drum. During the filling operation, the drum opening is surrounded by a hinged ventilation hood. Exhaust is discharged to the atmosphere following scrubbing (Bales 1978).

8. WASTE GENERATION RATES

The composition of selected waste streams from the production of epichlorohydrin were given in terms of lb. of waste/lb. of product (Gruber 1975), and are reported in

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* Dow Chemical Co. 1985: Personal communication.

Table 7-1. Overall waste generation rates for the whole industry, however, could not be determined due to the lack of sufficient data. Fractional waste generation (the percentage each waste represents of the total waste generated) was estimated based on available information and industry comments. These values are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

This section deals with the problem of how to reduce the volume and/or toxicity of the epichlorohydrin production process waste streams. Off-gas and HCl generation will not be considered in this report. HCl has various industrial uses and is a salable by-product; the off-gases, containing relatively minute amounts of substances such as allyl chloride, chlorine, and epichlorohydrin are flared.

9.1 Description of Techniques

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" has also been included. Good operating practices are defined as procedural or institutional changes which result in a reduction of waste. The following items highlight the scope of good operating practices:

- Waste stream segregation
- Personnel practices
  - Management initiatives
  - Employee training
- Procedural measures
  - Documentation
  - Material handling and storage
  - Material tracking and inventory control
  - Scheduling
- Loss prevention practices
  - Spill prevention
  - Preventive maintenance
  - Emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified. A summary of the source control methodology is given in Table 9-1. Sections below describe the listed methods.

9.1.1 Heavy and Light Ends from Allyl Chloride Synthesis Step

The reduction of the volumes of these effluent streams will be considered as waste minimization only to the extent that these streams are still land disposed. In the facilities which currently process these streams, e.g., recover HCl following thermal oxidation, source reduction methods may be viewed as either not applicable or as means to increase the allyl chloride yield.

Formation of heavy and light ends is governed by side reactions. In principle, the desired substitution reaction to form allyl chloride ($\sim 570^{o}$ F) is accompanied by: a low temperature ($< 400^{o}$ F) addition chlorination reaction, an unsaturated monochloride isomer formation, an unsaturated dichloride formation by further chlorination of allyl chloride, and by thermal degradation ($> 1100^{o}$ F) to tars, carbon, and benzene. The following source reduction methods were considered:

- Alternate reactor design.
  Present reactor design encompasses the features of a strongly backmixed plug flow reactor. A thorough review of the kinetic data for the reactions may reveal that the current degree of mixing can be improved with an attendant yield increase for allyl chloride. At one facility, reactor design modifications to provide better mixing resulted in a drastic decrease in the tars formation rate*. In evaluating different modification schemes, consideration should be given to staged addition of chlorine. Also, the concept of a fluidized bed reactor with inert solids (e.g., sand) appears worthy of consideration because of excellent mixing and thermal stability characteristics.

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* Dow Chemical Co. 1985: Personal communication

- Preheat of chlorine feed.
  It is postulated that curtailment of the low temperature addition reaction can be achieved through preheating of the chlorine feed (e.g., utilizing reactor effluent waste heat) prior to mixing with hot propylene. The preheat temperature of the propylene can be consequently decreased.

- Thermal oxidation with HCl and heat recovery.
  This efficient technique is extensively used in the integrated chlorohydrocarbon facilities. Energy recovery results in a lowered steam requirement, leading to lower boiler blowdown rates and associated wasteloads. Recovered HCl can be routed to oxychlorination units serving other processes (such as VCM or PCE/TCE). This technique may be viewed both as recycling or as source control, depending on the process boundary.

- Purified feed stock.
  In allyl chloride manufacturing, the propylene feed impurities usually encountered are water and propane (De Benedictis 1979). Water may react with chlorinated hydrocarbons to form undesirable by-products and may also provide a corrosive environment. Propane and other hydrocarbons are chlorinated to undesirable saturated chlorides. The level of feedstock purification required to offset the undesired byproduct formation can be worth re-assessing in light of increasing waste generation costs.

9.1.2 Heavy Ends from Epichlorohydrin Production

Heavy ends come from the epichlorohydrin fractionator and originate in the chlorohydroxylation reactor. A decrease in the volume of heavies production could be achieved through implementation of the following:

- Thermal oxidation with HCl and heat recovery.
  Currently this technique is extensively used in the highly integrated chlorinated hydrocarbon facilities.

- Alternate process routes.

  The alternate method for producing epichlorohydrin starts with the chlorination of acrolein to give 2,3-dichloroproprionaldehyde (Furman, Fiach, and Hearn 1958). Reduction of the aldehyde with sec-butyl alcohol (using aluminum sec-butoxide as a catalyst) yields glycerol and dichlorohydrin. Dehydrochlorination with lime then forms epichlorohydrin as is currently done. Epichlorohydrin can also be prepared by the epoxidation of allyl chloride with peracids (Phillips and Starcher 1957, Kellaetal 1974, Kleemann et al. 1971), perborates (Bruenie and Crenne 1965), or by epoxidation with tert-butyl hydroperoxide over vanadium (Sakan, Sano, and Hattori 1970), tungsten (Sakan, Sano, and Hattori 1970), or molybdenum compounds (Sakan, Sano, and Hattori 1970, Oshin, Shakhovtseva, and Krasotkina 1975) or by oxidation with air over a cobalt catalyst (Mokrousia, Oshin, and Tregar 1976). One route relying on chlorination of allyl alcohol to dichlorohydrin followed by epoxidation was patented in Japan. These alternate process routes may have proven to be economically unfavorable in the past. However, advancing technology and recent increases in disposal costs could warrant new investigations of economic feasibility for some of these alternate routes for new grass roots plants.

- Reevaluation of chlorohydroxylation reaction kinetics and reactor designs.

  Clear understanding of how byproducts (such as 1,2,3 -trichloropropane) are formed in the chlorohydroxylation reactor is necessary to examine low-waste alternative designs of the reactor (i.e., the designs which minimize byproduct formation). Such study may be warranted in light of increasing disposal costs.

9.1.3 Allyl Chloride Reactor Tars

The formation of these tars can be reduced by alteration of the reactor design, as discussed in Section 9.1.1. Provision for more mixing to eliminate stagnant areas in

the reactor resulted in the decrease of tar cleanup frequency from 10 days to 2 months at one facility*. The tars can be combusted for heat and HCl recovery in certain incinerator designs.

9.1.4 Miscellaneous Equipment Cleanup Wastes

Usually, the wasteloads associated with equipment cleaning are small and periodic in nature (once every 1 or 2 years). Further reductions may be obtained through:

- o Complete drainage of process piping or equipment prior to cleaning.
- o Use of non-stick (electropolished or Teflon**) heat exchanger tubes to reduce deposit clingage.
- o Use of in-process heat exchanger tube cleaning devices (Anonymous 1985a).
- o Lower process film temperatures and increased turbulence at the heat exchanger surfaces to reduce fouling rates.

All the suggestions listed above will have only a minor impact on overall waste generation, since equipment cleaning wastes are but a small fraction of the total waste. The reader is further referred to the separate study of process equipment cleaning in this appendix.

9.1.5 Spills and Leaks

As mentioned before, spills and leaks constitute a rather minor waste stream because of the extensive level of preventive maintenance practiced. Further source reduction is possible, in principle, through better operating practices (see separate process study entitled "Good Operating Practices"). Additionally, some consideration should be given to:

- o Replacing single mechanical seals with double mechanical seals on pumps or using canned seal-less pumps.

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* Dow Chemical Co. 1985: Personal communication

** Registered trademark of E.I. Du Pont.

- o Using leak detection systems and portable monitors.

- o Enclosed sampling and analytical systems.

9.2 Implementation Profile

The identified source control options require considerable engineering and economic analyses before implementation. The two U.S. producers of epichlorohydrin are both large organizations with excellent technical capabilities. Therefore, analyses of technical and economic feasibility are best performed by their resident technical staff. No process-specific source control implementation avenues have been identified.

9.3 Summary

Table 9-1 represents a summary of proposed source control methodologies for the epichlorohydrin manufacturing industry. Each method was rated for its effectiveness, extent of current use and future application potential. Based on these ratings, a current reduction index of 3.1 on a scale of 0-4 (78 percent) was derived, which is indicative of the high level of waste reductions already achieved by the epichlorohydrin industry. (The current reduction index represents the amount of waste that was reduced compared to the waste volume that would currently be generated without all the measures listed and their current level of application.) It appears that by implementing additional waste reduction measures, the amount of waste currently being generated can be further reduced to the level characterized by a future reduction index of 0.7 to 0.9 (18 to 22 percent reduction from current waste generation levels). Potentially, the most effective measures for achieving reductions in waste are those that are characterized by high value of the future reduction index. As shown in Table 9-1, these include: use of an alternate allyl chloride reactor design, further application of burning the chlorinated waste for HCl and heat recovery, additional purification of propylene feedstock, reevaluation of chlorohydroxylation reactor design and use of non-stick heat exchanger tubes.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE EPICHLOROHYDRIN MANUFACTURING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Heavy/Light Ends Allyl Chloride Production (*)	1. Alternate reactor design	2	2	3	2	2		1.5	0.8	0.8
	2. Preheat the chlorine feed	0	0	1	0	1		0.0	0.3	
	3. Recover the HCl/heating value	2	2	4	3	3		3.0	0.8	0.8
	4. Purify feedstock	1	1	2	1	2		0.5	0.8	0.8
	Overall	1.25	1.25	2.50	1 50	2.00	0.35	3.0	0.6	0.8
Heavy Ends Epichlorohydrin Production (*)	1. Recover the HCl/heating value	2	2	4	3	3		3.0	0.8	
	2. Use alternate process route	3	2	1	0	1		0.0	0.3	
	3. Re-evaluate chlorohydroxylation	0	0	2	0	2		0.0	1.0	1.0
	Overall	1.67	1.33	2.33	1.00	2.00	0.35	3.0	0.7	1.0
Tars Allyl Chloride Reactor (*)	1. Alternate reactor design	2	2	3	2	2		1.5	0.8	0.8
	2. Recover the HCl/heating value	2	2	4	3	3		3.0	0.8	0.8
	Overall	2.00	2.00	3.50	2.50	2.50	0.24	3.0	0.8	0.8
Equipment Cleaning Wastes (*)	1. Increase equipment drainage time	1	1	3	3	2		2.3	0.4	
	2. Lower heat exchanger film temperature	1	1	2	1	1		0.5	0.4	
	3. Non-stick heat exchanger tubes	2	1	3	0	2		0.0	1.5	1.5
	4. Use in-process H.X. cleaning devices	2	1	2	1	2		0.5	0.8	
	Overall	1.50	1.00	2.50	1.25	1.75	0.05	2.3	0.8	1.5
Spills and Leaks	1. Use double mechanical seals on pumps	1	1	3	4	2		3.0	0.0	
	2. Use leak detectors	3	3	2	3	1		1.5	0.1	0.1
	3. Enclosed sampling and analy. systems	3	2	2	3	1		1.5	0.1	0.1
	4. Use vapor recovery systems	2	2	4	4	1		3.9	0.0	
	Overall	2.25	2.00	2.75	3.50	1.25	0.01	3.9	0.1	0.1
All Sources	All Methods						1.00	3.1	0.7	0.9

(*) These waste streams include listed "F" and/or "K" RCRA wastes.

10. PRODUCT SUBSTITUTION ALTERNATIVES

There does not appear to be any viable alternative for epoxy resins, a principal consumer of epichlorohydrin. Epoxies have uniquely desirable physical properties, such adhesiveness combined with toughness and resistance to chemical attack. It would be difficult to find an epoxy substitute of comparable quality.

Approximately 19% of the crude epichlorohydrin produced is used to make synthetic glycerol. Glycerol has wide applications, as listed in Section 4. The alternative to synthetic glycerol is the glycerol obtained as a by-product during the production of soaps from animal and vegetable fats and oils (a principal source of glycerol prior to 1948). Alternatively, sorbitol offers a viable substitute for glycerol in pharmaceutical and cosmetic applications.

11. CONCLUSIONS

As is the case with other organic chemical processes, the epichlorohydrin industry appears to have reduced their wastes considerably by implementing the source control techniques noted. However, it is also apparent that moderate further reductions are possible. Based on the available information, it appears that the following methods deserve further consideration:

- Alternate allyl chloride reactor design to provide more mixing.
- Combustion of waste with attendant HCl and heat recovery.
- Use of purer feedstock.
- Reevaluation of kinetics and design for chlorohydroxylation reactor.
- Use of non-stick heat exchanger tubes.

The identified product substitution alternatives were natural glycerol from vegetable fats and oils instead of from epichlorohydrin, and use of sorbitol in place of glycerol.

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13. INDUSTRY CONTACTS

S.L. Arnold, Manager, Environmental Information Clearinghouse, Dow Chemical Co. Midland, MI.

1. PROCESS: INORGANIC PIGMENTS MANUFACTURE
2. SIC CODE: 2816
3. INDUSTRY DESCRIPTION

As defined by Standard Industrial Classification (SIC) 2816, the inorganic pigment industry includes establishments engaged in the manufacture of inorganic black pigments (except furnace and channel carbon black), white pigments, and colored pigments.

3.1 Company Size Distribution

In 1982, the industry included 106 establishments nationwide, and employed 11,200 people. Roughly 63% of the total work force was employed at 13 large establishments. Table 3-1 summarizes company size distribution.

Table 3-1 1982 Company Size Distribution

	No. of employees per facility				
	Total	1-19	20-99	100-499	500+
No. of establishments	106	43	39	17	7
No. of employees	11,200	400	1,800	4,100	4,900

Source: 1982 Census of Manufacturers (USDC 1985).

3.2 Principal Producers

The principal producers of inorganic pigments in the U.S. include the companies listed below (Versar 1980, Williams et al. 1976):

American Cyanamid Co.
CIBA-GEIGY Corp.
E.I. du Pont de Nemours & Co., Inc.
Hercules
Kerr-McGee Corp.
NL Industries, Inc.
SCM Corp.

3.3 Geographical Distribution

The geographical distribution of inorganic pigment plants is shown in Figure 3-1 and Table 3-2 below. Half of the total number of plants are located in just five states, and the majority are clustered in the industrialized regions stretching between Illinois and New Jersey.

Table 3-2 Geographical Distribution of Inorganic Pigment Plants by EPA Region

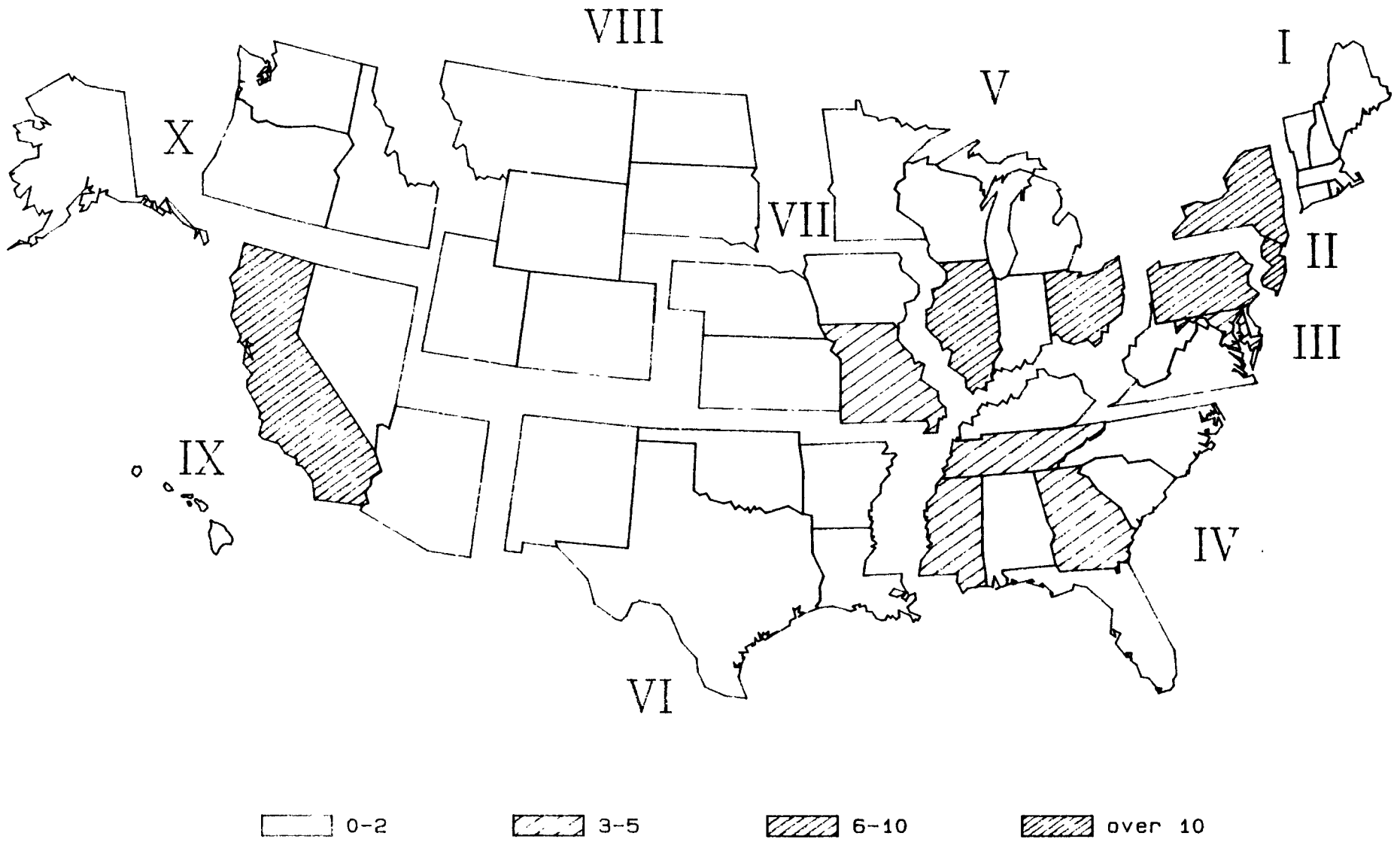
EPA Region	Number of Establishments
I	-
II	24
III	16
IV	11
V	22
VI	-
VII	3
VIII	-
IX	10
X	-
National	106(a)

Source: 1982 Census of Manufacturers (USDC 1985).

(a) The discrepancy between the national total and the sum of the ten EPA regions listed above is due to the exclusion of establishments in states with less than 150 employees.

4. PRODUCTS AND THEIR USES

Inorganic pigments include black, white, colored, colorless, and metallic pigments and are used for a variety of decorative, protective, and functional purposes. They are used for automotive finishes, industrial coatings, oil and latex paints, and many paper, plastic, rubber, glass, cement, and porcelain products (Scheik 1982). A list of the various inorganic pigments produced in the U.S. is given in Table 4-1.



Roman numerals show EPA regions

Figure 3-1 Inorganic Pigment Plants in the U.S.

Table 4-1 Inorganic Pigments Produced in the U.S.

Product	Quantity Produced (thousands of tons)
Titanium pigments	886.0
Other white opaque pigments, including basic carbonate and sulfate pigments, white lead, excluding white lead in oil	6.6
Zinc oxide pigments	128.6
Chrome colors	
Chrome oxide green	4.0
Chrome yellow and orange	21.0
Molybdate chrome orange	6.2
Zinc chromate	--
other chrome colors	--
White extender pigments, including barytes, blanc fixe, whiting colors and lakes and toners	51.1
Color pigment other than chrome colors, lakes, and toners	
Iron oxide pigments	--
Colored lead pigments	--
Carbon black (excluding furnace and channel carbon black and charcoal)	5.0
Cadmium sulfide pigments	2.9
Ceramic colors and all others	--

Source: 1982 Census of Manufacturers (USDC 1985) and industry comments.

5. RAW MATERIALS

The raw materials used in the production of inorganic pigments consist of a broad range of chemicals including basic organic and inorganic chemicals as well as a variety of ores and minerals. These materials, along wih their respective consumption rates, are listed in Table 5-1.

Table 5-1 Raw Materials Used in the Production of Inorganic Pigments for 1982

Raw Material	Consumption Rate (thousands of tons)
Organic chemicals	
Alcohol, ethyl	*
Other alcohols	*
Plastic resins	8.3
Other organic chemicals	*
Inorganic chemicals	
Acids, except spent acids	
Hydrochloric acid	13.6
Hydrofluoric acid	*
Nitric acid	5.7
Phosphoric acid	1.0
Sulfuric acid	254.8
Ammonia	5.1
Chlorine	304.1
Phosphorus	*
Sodium carbonate	*
Sodium hydroxide	62.1
Salt in brine	*
Acetylene and other industrial gases compressed and liquified, including argon, carbon dioxide, nitrogen, nitrous oxide, etc.	*
Crude materials	
Bauxite	*
Phosphate rock	*
Sulfur	*
Sulfuric acid sludge	*
Zinc and zinc based alloy refinery shapes	*
Iron and ferrous alloy ores	*
Nonferrous metal ores	*
Crude non-metallic minerals	*

* No data
Source: 1982 Census of Manufacturers (USDC 1985).

6. PROCESS DESCRIPTION

There are a variety of processes used to produce the pigments listed in Table 4-1. Since titanium dioxide (TiO_2) is the most widely used inorganic pigment, the

remainder of this study will focus on the production of TiO_2 and associated source reduction practices.

Titanium dioxide is produced by two major processes - the sulfate process and the chloride process. While both processes are widely used at present, the chloride process is likely to displace the sulfate process in the future. The sulfate process has been hurt by a combination of economic, environmental and market forces. Environmental problems and waste disposal costs associated with the large amounts of spent acid and iron salt wastes which are produced during the sulfate process have resulted in the closure of certain U.S.-based plants (Ryser 1985). In addition, TiO_2 pigment from the chloride process is preferred for use in paint products, which accounts for roughly half of TiO_2 use. For these reasons, further discussion will be limited to the production of TiO_2 by the chloride process.

In the chloride process, two types of raw materials may be used. Ilmenite ore, which contains 40-70% TiO_2, is one raw material. The other is either rutile ore or upgraded ilmenite ore, both of which contain more than 90% TiO_2 (Versar 1980, USEPA 1980a, Ryser 1985). The ore is mixed with coke and reacted with chlorine at 800 to 1000°C in a fluidized bed reactor. The reaction produces titanium tetrachloride, carbon dioxide, carbon monoxide, iron chlorides, and small amounts of other metal chlorides. The gases are cooled stepwise to remove impurities. The first cooling step lowers the temperature to 250°C to remove iron and other heavy metal chloride. These are removed as solids by filtration. Further cooling of the remaining gases to ambient temperatures condenses the titanium tetrachloride and some dissolved chlorine. The uncondensed gases remaining include carbon monoxide, carbon dioxide, unreacted chlorine, hydrochloric acid, some titanium tetrachloride, and other trace gases. The uncondensed gas stream is scrubbed before being discharged to the atmosphere or incinerated for its CO (heating) content. The condensed titanium tetrachloride stream contains impurities such as aluminum chloride and silicon tetrachloride which are removed through distillation. Copper and/or proprietory organic complexing agents are added during the distillation step to aid in the decomposition of trace phosgene (present as an impurity) and to help separate titanium tetrachloride from other chlorides.

The purified titanuim tetrachloride product is then oxidized with air or oxygen at 1500°C to produce titanium dioxide and chlorine gas. The chlorine gas is often

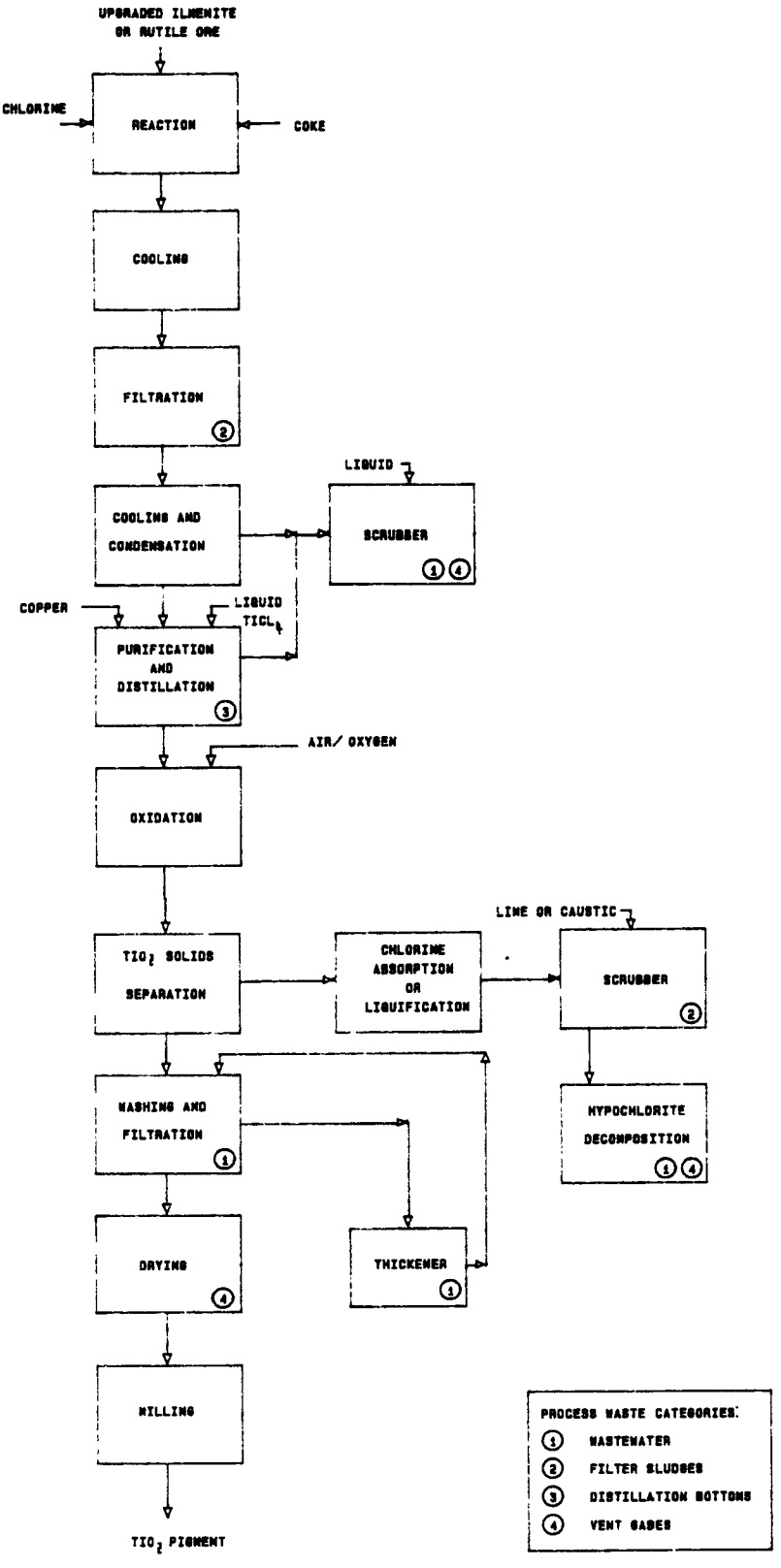


Figure 6-1 Titanium Dioxide Production by the Chloride Process

recycled to the chlorination reactor. The solid titanium dioxide is separated from the gas phase using filters, cyclones, or other proprietary methods. The gases from the oxidation reaction are scrubbed with lime or caustic soda before being discharged to the atmosphere. The solid titanium dioxide is then washed with alkali to remove hydrochloric acid and residual chlorine. It is then dried, milled, coated with an inorganic oxide such as alumina to increase its weathering resistance, and packaged (Versar 1980, USEPA 1980a).

7. WASTE DESCRIPTION

The major waste streams along with their process origins and compositions are listed in Table 7-1. Air pollutants are generated during oxidation, distillation, and drying. The major air pollutants produced include titanium tetrachloride, hydrogen chloride, and carbon monoxide from the chlorination and oxidation reactions, as well as chlorine and particulates from drying and milling. The gases from the chlorination and oxidation reactions are normally treated in wet scrubbers producing a wastewater stream which must undergo further treatment.

Wastewater is also generated from washing, filtering, drying, milling, and equipment cleaning, and from processing of distillation bottoms. Wastewater is typically treated by in-plant systems using such conventional treatment processes as pH adjustment, precipitation, and clarification. At plants where ilmenite ore with a high iron content is used as a raw material, large amounts of acidic iron chloride wastes are produced. This waste stream has been disposed of by deep-well injection or ocean dumping at some locations. Solid wastes produced during the chlorination reaction include unreacted ore, coke, and metal salts. These are either recycled or disposed of in landfills. For those plants using ilmenite with a high iron content, ferric chloride waste poses a major disposal problem. However, markets exist for the use of ferric chloride as a flocculant or a wastewater treatment chemical. In these application, ferric chloride can be used to clarify drinking water, to treat sewage, and to remove phosphorus from wastewater (Du Pont 1985a). Du Pont presently recovers and sells roughly 100,000 tons per year of ferric chloride from one of its titanium dioxide plants. While the supply of ferric chloride appears to be greater than its demand as a wastewater treatment chemical, this market does absorb large quantities of the waste. Ferric chloride produced by titanium dioxide plants competes with the ferric chloride

Table 7-1 Manufacturing Wastes From TiO_2 Production (Chloride Process)

No.	Waste Description	Process Origin	Composition	Concentration (lb/1000 lb product) 95% TiO_2 ore	Concentration (lb/1000 lb product) 65% TiO_2 ore	RCRA Codes
1.	Chlorinator wastes	Chlorination reactor	unreacted ore	16	25	--
			coke	37	68	
			iron chlorides	2	380	
			other metal chlorides	-	-	
			titanium tetrachloride	25	-	
			HCl	130	-	
2.	Chlormator scrubber wastes	Chlorination gas scrubber	titanium tetrachloride	25	-	--
			HCl	50	-	
			chlorine	-	-	
			phosgene	-	-	
3.	Distillation	Distillation	metal oxides and chlorides	-	-	--
			organic complexing agents	-	-	
4.	Oxidation scrubber wastes	Oxidation tail gas scrubber	hypochlorite	-	-	--
5.	Finishing operations wastes	Washing, filtering, drying, milling	titanium dioxide	10	-	--
			$NaCl + Na_2SO_3$	16	-	

produced by the steel industry during steel pickling operations for the wastewater treatment market.

8. WASTE GENERATION

The 1980 waste generation rates from the production of titanium dioxide by the chloride process are given in Table 7-1. The exact types and quantities of wastes produced are dependent upon the raw ore used in the process. Waste rates for processes using high quality ore (95% TiO_2) and lower quality ore (65% TiO_2) are both given. The major difference in waste output between the two is the amount of ferric chloride produced. Plants using lower grade ilmenite ores produce much greater amounts of iron chloride waste than do plants using high grade ore.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

The wastes which are produced during the manufacturing of titanium dioxide by the chloride process are listed in Table 7-1. Various source reduction methods available for reducing these waste streams are discussed below.

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" have also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel Practices
  - Management initiatives
  - Employee training
- o Procedural measures
  - Documentation
  - Material handling and storage
  - Material tracking and inventory control
  - Scheduling

- o Loss prevention practices
  - Spill prevention
  - Preventive maintenance
  - Emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Ferric Chloride Waste

As mentioned previously, for plants using ores with high iron content, the ferric chloride produced during the chlorination reaction poses a major disposal problem. In addition, chlorination of the unwanted iron represents an economic disadvantage since the chlorine must then be disposed of as waste. Source reduction measures to reduce the amount of ferric chloride produced include:

- o Use of high-purity ores.

  The use of a high purity ore will minimize the amount of impurities entering the process, greatly reducing waste generation rates. As discussed earlier, two types of ore, ilmenite and rutile, have traditionally been used to produce titanium dioxide by the chloride process.

  Plants utilizing ilmenite ore generate large amounts of iron chloride wastes. Ilmenite ore contains 40-70% titanium dioxide and large amounts of iron. During the chlorination reaction this iron is converted to iron chlorides which are either sold as a by-product (see below) or disposed of as a waste, often by deep well injection.

  Rutile ore, containing greater than 90% titanium dioxide and only small amounts of iron, results in substantially less waste generation. Rutile ore however, is much less abundant than ilmenite ore, and is more expensive. To achieve the benefits of a higher purity ore, ilmenite can be blended with ferro-titanium slag to produce a raw material of roughly 75% titanium dioxide (McNaulty 1986).

A third type of ore called anatase (25% titanium-dioxide) is being tested for use at a few titanium dioxide facilities (Ryser 1985). The main advantage of using anatase is economic since it may only cost 10% as much as rutile ore. The process, designed by Du Pont, is a modification of an old chloride route developed several decades ago. No other technical information is available and the comparative waste generation characteristics are unknown.

- Recovery of valuable products.

  Chlorine can be recovered from ferric chloride by oxidizing the material with oxygen or air in a fluidized bed reactor. Based on pilot plant tests, 99% recovery of chlorine was achieved (Ogawa 1980). An important part of the process was that the ferrous chloride was mixed with iron oxide particles (also produced in the reaction) before being introduced into the reactor. The oxide acted as a catalyst and increased the reaction rate. The major disadvantage of the process, however, was low conversion of oxygen (only 75 percent). Oxygen, if present with the recycled chlorine, would increase the amount of coke required in the chlorination reactor and the amount of off-gas generated. Going to a larger oxidation reactor was expected to increase the conversion of oxygen to 85 percent. It was reported that a Canadian firm attempted to recover chlorine from ferric chloride in the early 1970's but that no current work is being performed*. Currently, Du Pont continues to investigate this option but their efforts have not yet overcome the difficulties encountered in previous attempts.

  Another process for converting ferric chloride waste into valuable products is to first slurry the waste with water and then spray the slurry into a roasting furnace operating at 1000°C (Setoguchi 1980). The reaction produces iron oxide and HCl containing gases which are scrubbed to produce 18 weight percent hydrochloric acid. This acid can be used elsewhere in the facility or further processed to produce chlorine and hydrogen (for example, using the Kel-Chlor or electrolysis process). Fuel for operating the roasting furnace can be taken from the chlorination reactor off-gas which contains a high level of CO.

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*Confidential source 1985: Personal communication.

- Ore pretreatment.

  Ilmenite is the major type of titanium ore available domestically. As noted above, ilmenite often has a high iron content which leads to the generation of iron salts as a waste. One possible way to reduce this waste stream is to pretreat the ore prior to digestion to remove the iron. Ilmenite can be converted to an alkaline earth titanite, such as sodium titanate. When sodium titanate is used in the chloride process, the waste produced is sodium chloride or sodium sulfate, which leaves the process as inert dissolved solids (Versar 1980). While this process is attractive environmentally, it may not be practical from an economic standpoint*.

  Other methods of upgrading ilmenite ore for TiO_2 production are the Benilite process (which has been commercialized in India, Japan, and Taiwan) and the Murso process. In both processes, iron is leached out of the ore using hydrochloric acid thereby producing a feed material of greater than 90% titanium dioxide. After the iron is leached out as ferrous chloride, it is converted to iron oxides and hydrochloric acid. The hydrochloric acid can be reused within the process (Versar 1980). Pretreatment of the ore (oxidation and reduction) and addition of ferrous chloride to the hydrochloric acid leach solution have been reported to increase or improve the leachability of the ore and reduce fines generation (Sinha 1980).

9.1.2 Scrubber Wastes

Air emissions are commonly treated in a wet scrubber, producing substantial amounts of wastewater. In the production of titanium dioxide by the chloride process, scrubber water accounts for as much as 20 percent of the total wastewater stream (USEPA 1980a). Unreacted chlorine gas from the chlorination reactor is removed from the tail gas by scrubbing with either water or caustic. Reduction of chlorine content in the tail gas will result also in reduction of scrubber wastewater, treatment chemical usage and chlorine loss. The discharge of unreacted chlorine in the tail gas can be reduced or eliminated by chlorine liquefaction achieved by pressurization and subsequent refrigeration to condense chlorine from the tail gas (USEPA 1980a).

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*E.I. du Pont de Nemours & Co. 1986: Personal communication.

9.1.3 Filtering and Washing Wastes

The ore impurities will at some point have to be separated from the desired product, resulting in a waste stream which must be treated. A substantial portion of wastewater generated in TiO_2 plant is from the rinsing and washing of the pigment. Rinsing and washing serves the purpose of removing residual chlorine and hydrogen chloride, soluble salts, and other impurities from the final product. The amount of impurities is largely controlled by ore composition and the efficiency of the upstream distillation process to purify titanium tetrachloride. However, the use of water can be reduced using countercurrent rinsing and the amount of pigment carry-over can be reduced by using more efficient filtration.

9.2 Implementation Profile

The major source of waste from titanium dioxide pigment manufacturing is simply the impurities separated out from the ore. Thus, the most important source control methods are concerned with the quality of ore used. The use of high-purity ores reduces the amount of impurities introduced into the process. However, a manufacturer may have little control over the quality of the ore which is used if the availability of high-puriy ore is limited. In this case, ore pre-treatment and the recovery of chlorine and iron oxide gain significance. The use of efficient rinsing and washing techniques for product purification along with the reduction of scrubber wastes through chlorine recovery from the tail gas are, in essence, water conservation measures and, as such, may not be prime waste minimization issues of current environmental concern.

9.3 Summary

The waste sources and their respective source control techniques are summarized in Table 9-1. The ratings listed in this table are based on a scale of zero to four and are used to evaluate each technique for its waste reduction effectiveness, extent of current use, and future application potential. The ratings were derived by the project staff based on the available information.

It appears that the current level of waste minimization in titanium dioxide manufacturing based on the chloride process is significant. This is evidenced by the current

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE TITANIUM DIOXIDE MANUFACTURING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Ferric Chloride Waste	1. Use high-purity ore	3	3	4	2	1		2.0	0.5	
	2. Recover products from waste	2	2	3	0	1		0 0	0.8	0.8
	3. Pretreat ore to remove iron	3	3	2	2	2		1.0	0.5	
	Overall	2.67	2.67	3.00	1.33	1.33	0.05	2.0	0.6	0.8
Scrubber Wastes	1 Chlorine liquifaction for reuse	1	2	2	2	1		1.0	0.3	0.3
	Overall	1 00	2.00	2.00	2.00	1.00	0.20	1.0	0.3	0.3
Filtration and Washing Wastes	1. Use more efficient filters	1	2	1	2	2		0.5	0.3	
	2 Use efficient washing/rinsing methods	2	2	3	3	1		2 3	0.2	
	3. Process control/automation	1	1	2	2	2		1.0	0.5	0.5
	Overall	1.33	1.67	2.00	2.33	1.67	0.75	2.3	0.3	0 5
All Sources	All Methods						1.00	2.1	0.3	0.5

(*) These streams include listed "F" and/or "K" RCRA wastes.

reduction index (CRI) of 2.1 (53 percent), which is a measure of reduction of waste that would have been generated if none of the listed methods were applied at their current level of use.

Future reductions appear to be rather modest as evidenced by the future reduction index (FRI) of 0.3 and 0.5 (8 to 12 percent). FRI is the measure of waste reduction achievable through the implementation of the listed techniques to their full rated potential. From the standpoint of future application, the most promising source control techniques found were product recovery from waste (Cl_2 and Fe_2O_3), ore pretreatment to remove iron, and use of high purity ore.

10. PRODUCT SUBSTITUTION ALTERNATIVES

10.1 Paint Usage

Paint and paint-related products, such as automotive finishes, account for a large portion of total titanium dioxide pigment usage. No substitute for titanium dioxide was identified in paint pigment application. However, any reductions in the use of paint will have a direct impact on the demand for titanium dioxide. For additional discussion of this issue the reader is referred to the study of paint manufacturing included in this appendix.

10.2 Paper Products

Paper products account for roughly 18% of the total use of titanium dioxide, which is the most widely used inorganic pigment (USEPA 1980a). In paper manufacturing, titanium dioxide (TiO_2) is used as an opacifier. In place of TiO_2, alumina or silica clays have been tried, however the main advantage of TiO_2 over the other substances is that it has a superior reflectance.

11. CONCLUSIONS

The facilities using the chloride process for production of titanium dioxide appear to have minimized their waste significantly by using high-purity ore. Water use was reduced by the application of efficient washing and rinsing techniques. Any future reductions appear to be modest, in the range of 8 to 12 percent, primarily resulting

from wider adoption of ore pretreatment, use of high purity ore and, possibly, recovery of Cl_2 and Fe_2O_3 from $FeCl_3$ waste stream (potentially, the most effective technology which has not yet been commercialized).

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13. INDUSTRY CONTACTS

Confidential Source

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1. PROCESS: METAL SURFACE FINISHING
2. SIC CODE: 3471
3. INDUSTRY DESCRIPTION

Metal finishing is a part of the plating and polishing industry classified under Standard Industrial Classification (SIC) 3471. This industry is comprised of establishments primarily engaged in all types of electroplating, plating, anodizing, coloring, and finishing of metal and formed products for the trade. Most of the work performed by this industry is done on materials owned by others. Though metal surface finishing is classified under SIC 3471, metal finishing operations are performed by many other industries included in SIC groups 34 through 39 (USEPA 1980). The metal finishing process includes some 44 unit operations and only the metal surface finishing operations that use chemical means are discussed in this report.

3.1 Company Size Distribution

Since metal surface finishing operations are performed by various industries classified under many SIC codes, company size distribution data for metal surface finishing as an industry was not separately available. In 1980, there were approximately 160,000 manufacturing facilities in the U.S. which were covered by the metal finishing category (USEPA 1980). These facilities varied greatly in size, age, and number of employees. They ranged from very small independent job shops with less than ten employees, to small shops within large corporations, to large facilities employing large work forces.

3.2 Principal Producers

The metal surface finishing industry is dominated by small job shops employing less than 20 employees each. There are no major producers who control a large share of the market.

3.3 Geographical Distribution

The geographical distribution of the metal surface finishing industry was not available due to the reasons stated above.

4. PRODUCTS AND THEIR USE

The metal surface finishing industry deals mostly with the treatment of metallic or non-metallic products manufactured by others. Each product requires a specific process sequence to obtain the desired physical, chemical, or aesthetic properties desired by the user. The principal products of the metal surface finishing industry include:

Printed circuit boards	Kitchen utensils
Coil coating	Jewelry
Automotive parts	Mechanical (non-automotive) parts

5. RAW MATERIALS

Reagents — phosphoric acid, secondary or tertiary metal phosphates, sodium dichromate, sodium nitrate, sodium cyanide, barium chloride, sodium chloride, sodium carbonate, sodium cyanate, ammonia, silicon tetrachloride, zinc oxide, chromic acid

Accelerators — quinoline, toluidine, nitrophenols, various oxidizing agents such as peroxides, and sulfites

Metals — zinc, aluminum, chromium, cadmium, magnesium, iron, nickel, copper, silver, molybdenum, vanadium, tungsten

Alloys — tin, lead-tin alloys, bronze, brass

6. PROCESS DESCRIPTION

Metal surface treatment consists of various processes such as electroplating, electroless plating, anodizing, chemical conversion coating, cleaning, etc. (USEPA 1980, BCL 1976, Schneberger 1981, Durney 1984). Since electroplating and metal surface cleaning are discussed in separate studies in this appendix, this study considers only chemical surface treatments such as electroless plating, chemical

conversion coating, etching, chemical milling, and some forms of case hardening treatment. Metal surface treatment is performed mainly to modify the metal surface to be less reactive and more corrosion-resistant and is dependant on the type of required surface modification. All the metal surface treatment processes have three basic steps: surface cleaning or preparation, surface treatment, and rinsing or post-finishing operations. The cleaning and post-finishing operations are specific to the surface treatment method used. The following sections describe various surface treatment methods with the exception of coil coating. All chemical surface treatment operations are essentially batch operations, where the metal object is dipped in a bath containing various reagents to achieve the required surface modification.

6.1 Electroless Plating

Electroless plating allows for the deposition of metal on an object's surface without the use of external electrical energy. This is achieved by a chemical reduction process which depends upon the catalytic reduction of a metallic ion in an aqueous solution. This process has found widespread use due to several advantages over conventional electroplating which include ability to produce a uniform coat on all areas of the part regardless of its geometry without the need to supply external electrical energy. Copper and nickel electroless plating are the most common.

The basic ingredients of electroless plating solutions are a source of metal ions (generally copper or nickel), a complexing agent to maintain ions in solution at the operating pH value, a compatible reducing agent, a material to adjust the pH of the bath, and stabilizers, wetters, stress relievers, etc. Table 6-1 lists the bath constituents for copper and nickel electroless plating operations.

The electroless plating operation consists of cleaning the object surface, immersing it in a bath containing the previously described constituents for a specific period of time, and then rinsing the object (after removal from the bath) to remove process solutions adhering to the surface.

Plating bath solutions last only a few hours because catalytic particles precipitate in the bath. The bath life is usually increased by periodic filtration, and by the addition

Table 6-1 Bath Constituents for Copper and Nickel Electroless Plating

Function	Copper Plating Operation	Nickel Plating Operation
Metal ion source	Cupric sulfate (3-15 g/l)	Nickel chloride, nickel sulfate, nickel sulfamate, nickel hydrophosphite
Complexing agent	Rochelle salt (sodium potassium tartarate, ethylenediaminetetracetic acid (EDTA), sodium salts of EDTA, nitrilotriacetic acid, gluconic acid, gluconates, triethanol amine, n-hydroxy ethylene diamine tetracetate (20-50 g/l).	Lactic acid, dicarboxylates
Reducing agent	Formaldehyde, paraformaldehyde, trioxane, dimethylhydantoin, sodium and potassium borohydride.	Sodium hyposphosphite
pH adjustor	Sodium or potassium hydroxide	Sodium or potassium hydroxide
Stabilizers	2-mercaptobenzothiazole, thiourea, methanol	Molybdic acid anhydride, arsenious acid, hydroxyl amino sulfate, hydrazine.
Other additives	Water soluble metal cyanides, polysiloxanes, methyl dichloro silane	Thiourea, soluble fluorides, alcohol sulfonates, ethylene oxide derivatives, sodium sulfate.

Source: Development Document for Effluent Limitation Guidelines (USEPA 1980).

of stabilizers. The bath is eventually dumped thereby generating a waste stream. Other waste streams are generated by rinsing operations and periodic cleaning of the process equipment. Other electroless plating operations, such as vapor deposition, are purely physical operations and are not considered in this report.

6.2 Chemical Conversion Coating

This operation includes phosphating, chromating, metal coloring, and passivating. The coating deposited on metal objects is for decorative or corrosion protection purposes, and in some instances to prepare the surface for painting. The mode of operation and waste generation are similar to the electroless plating operation described in Section 6.1. The following sections discuss the four different chemical conversion coating methods listed above.

6.2.1 Phosphating

Phosphate coatings are formed on the surfaces of iron, steel, galvanized steel, aluminum, and electrodeposited zinc and cadmium to promote adhesion of organic coatings, to retard interfacial corrosion, to retain and enhance the performance of corrosion resistant oils, and to assist in cold deformation processes. Small parts are coated in barrels immersed in the phosphating solution and large parts are spray coated or continuously passed through the phosphating solution. The object to be coated may be dipped successively in a series of processing tanks.

The phosphating solution consists of a phosphoric acid solution of metal dihydrogen phosphate. The coating time and temperature depends on the type of metal to be coated and whether a spray or immersion coating scheme is used. Sometimes accelerators (to improve quality), stabilizers (to prolong bath life) and oxidizing agents (to control the coating rate) are added to the phosphating solution.

There are certain parameters, such as the ratio of free to combined phosphoric acid, total acid, metal-ion concentration, accelerator concentration, and the process temperature that must be controlled to achieve a suitable coating and maintain the

integrity of the bath. The coated object, after phosphating, may be given a conditioning rinse with dilute chromic and/or chromic-phosphoric acid for surfaces to be protected against corrosion, or an alkaline rust-inhibiting treatment for objects to be cold-deformed. Concerns about the environmental effects of chrome have led to the development of chrome-free rinses. Though these are less effective than their chrome-containing counterparts, they are suitable for applications where corrosion is not a major concern.

6.2.2 Chromating

Chromate coatings are most frequently applied on zinc, cadmium, aluminum, magnesium, copper, brass, bronze, and silver to minimize rust formation and to guarantee paint adhesion. Chromate-type conversion coatings are produced primarily by a simple immersion process although a spray or brush treatment can be used.

The chromating solution consists of chromic acid, one or two mineral acids such as sulfuric or nitric, and often some activating compounds. Chromate conversion coatings are formed because the metal surface dissolves to a small extent, causing a pH rise at the surface-liquid interface. This results in the precipitation of a thin complex chromium metal gel on the surface, composed of hexavalent and trivalent chromium and the coated metal itself. This gel is normally soft when formed and must be handled carefully. After drying, the coating becomes hard and relatively abrasion-resistant.

The thickness and color of the chromate coating depends on the solution composition, temperature, pH, and the length of treatment. The coated object is usually rinsed with cold water containing sodium hydroxide or sodium carbonate to provide a clear noniridescent coating. This is followed by a warm water rinse to prevent the removal of the coating.

6.2.3 Metal Coloring

While coloring of steel, copper, aluminum, and their alloys is done primarily for aesthetic purposes, this surface treatment often imparts other favorable properties such as improved corrosion resistance and better abrasion and wear characteristics. The coating operation is primarily of the immersion type.

Many formulations are available for the coloring of metals and most of them are proprietary. The major coloring process for steel uses a treatment solution of sodium hydroxide and sodium nitrate in water. The processing temperature may vary from 275-320°F, and the immersion time may vary from 5 to 30 minutes. The coating color and characteristics are largely a function of the alloy being treated, surface characteristics, concentration of the bath, temperature, and immersion time.

6.2.4 Passivation

Passivation refers to forming a protective film on metal, particularly stainless steel and copper, by immersion in an acid solution. Stainless steel is passivated to dissolve embedded iron particles and to form a thin oxide film on its surface. A typical treatment solution for stainless steel is nitric acid or nitric acid with sodium dichromate. Copper is passivated using a solution of ammonium sulfate and copper sulfate.

6.3 Chemical Etching

Chemical etching is used to produce specific design configurations and tolerances on metallic or metal-clad plastic (printed circuit boards) by controlled dissolution of the metal with chemical etchants. Typical etching solutions are ferric chloride, nitric acid, ammonium persulfate, chromic acid, cupric chloride, hydrochloric acid, etc. "Bright dipping" is a special form of chemical etching used to remove oxide layers from ferrous and non-ferrous materials.

6.4 Cyaniding

Cyaniding is a type of case hardening that produces a hard surface on a metal whose core remains relatively soft. The product is a hard, wear-resistant surface backed by a strong, ductile, and tough core. Carbon and alloy steels are usually immersed in the cyaniding bath for a specific period of time to achieve the required degree of surface hardening.

The most common cyaniding solution consists of 30 percent sodium cyanide, 40 percent sodium carbonate, and 30 percent sodium chloride. Baths containing 97, 75, and 45 percent sodium cyanide are also used. Oxygen from the air oxidizes the sodium

cyanide to sodium cyanate which, at high temperatures, decomposes to form nascent carbon and nitrogen. The carbon and nitrogen are absorbed by the steel, which increases surface hardness. The processing temperatures may vary from 1200-1350°F for low penetration to 1650-1725°F for high penetration. A combination treatment using high temperature immersion followed by low temperature immersion is also used.

The depth of surface that is hardened is controlled by the temperature and the cyanide content. As drag-out and carbon depletion occur, special salt compositions are added to replenish and regenerate the bath. At the end of the treatment, the objects are immersed in a water or oil bath, where quenching and rinsing is accomplished simultaneously. The quench water is potentially hazardous and is treated for cyanide destruction followed by clarification prior to discharge. The quench oil is also potentially hazardous and is disposed of by incineration.

7. WASTE DESCRIPTION

The primary wastes associated with metal surface finishing, along with their process sources, are listed in Table 7-1. The wastes produced in metal surface finishing operations come mainly from two sources: dumping of process tanks, and rinse waters used to wash off process solutions adhering to the product surface or entrapped in the crevices due to the shape of the product piece (Durney 1984, AESI 1981, CP Staff 1984). Additional waste is generated as a result of process solution filtering. The process solutions are periodically filtered to remove precipitated metals and are reused. These filtered solids are mixed with solids removed from the rinse waters and are either landfilled or sold for metal reclamation.

Other wastestreams include spills and leaks plus stripping wastes.

Spent Bath Solution

The activity of the plating solution decreases with time due to the precipitation of salts and depletion of constituents. After 3-6 regeneration cycles, the bath is eventually discharged*. This waste stream usually contains cyanides or metallic

*National Association of Metal Finishers 1985: Personal communication.

Table 7-1 Metal Surface Finishing Wastes

No.	Waste Description	Process Origin	Composition	RCRA Code
1.	Spent bath solution	Dumping of the process solutions after depletion or loss of activity.	cyanides, cyanide complexes, hexavalent chrome, copper, nickel, zinc, cadmium, and other metals and their salts in water	F011
2.	Waste rinse water	Rinsing treated objects, equipment cleaning, quenching of case hardened steel.	same as spent bath solution	--
3.	Filter waste	Filtration of process solution, spent baths, and treated waste rinse water.	Complexes of various metals, cyanides, etc.	F010 F012
4.	Spills and leaks	Overflows and leaks from various process equipment	same as (1)	--
5.	Stripping waste	Removal of coatings from improperly treated objects.	not available	--

complexes. In the recent past, this stream was treated together with the rinse water stream. However, the need for obtaining the necessary permits and also the perceived regulatory compliance difficulties have discouraged treatment of spent baths*. This stream is often sent off-site for disposal.

Waste Rinse Water

Rinse water is used to wash off process solutions adhering to the product surface or entrapped in its crevices due to its geometrical shape. The rinse water stream is usually discharged to municipal treatment facilities with or without any treatment, depending on its composition. The treatment procedure includes oxidative destruction of cyanides reduction of chromates, neutralization, and solids removal.

Filter Waste.

The filtration step in the regeneration of plating solution and the solids removal in rinse water treatment each generate a solid waste. These solids contain oxides or complexes of metals and are either landfilled or sent off-site for metal reclamation.

Spills and Leaks

The overflow and leaks from various process equipment are usually mixed with the rinse water stream and disposed of as explained above.

Stripping Waste

Before coating an object, the previous coatings on it are removed by a striping operation. This is also done to remove coatings from an improperly coated object. In small job shops, the same stripping solution could be used for removing different types of coating. The disposal of the spent bath from such operation is similar to that of the spent baths discussed earlier. The rinse waters are usually discharged to municipal treatment facilities with or without treatment. The untreated streams may contain various cyanides and cyanide complexes, hexavalent chrome, copper, nickel, zinc,

*Westinghouse Electric Corporation, 1985: Personal communication

cadmium and other metals. The treatment includes oxidative destruction of cyanides, reduction of chromates, neutralization, and solids removal. The treatment sludge is expected to be landfilled. Spills and overflows that occur can be mixed and treated with other liquid wastes and treated as discussed.

8. WASTE GENERATION RATES

Since metal finishing operations are often performed along with electroplating and other operations, the waste generation rates specifically attributable to metal finishing are difficult to determine. No waste generation data were in evidence at the time of the final document preparation. While no specific waste generation rates were reported, fractional rates were estimated by project staff based on the available information and engineering judgements. These values are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

The list of individual waste streams and sources and their corresponding source reduction methods is presented in Table 9-1. The following sections discuss the various waste reduction methods based on a literature survey and industry contacts.

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" has also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- Waste stream segregation
- Personnel practices
  - management initiatives
  - employee training
- Procedural measures
  - documentation
  - material handling and storage
  - material tracking and inventory control
  - scheduling

- o Loss prevention practices
  - spill prevention
  - preventive maintenance
  - emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Spent Bath Solutions

Most of the metal surface finishing operations are performed by immersing an object into tanks containing specific reagents. Due to the precipitation of salts and depletion of constituents, the bath becomes ineffective and must be regenerated or discarded when necessary. This waste, containing cyanide, cyanide complexes of metal, and other metallic complexes, is often sent to a treater for disposal. The following methods could reduce this waste stream:

- o Extending bath life.

  During the surface treatment operation, many insoluble salts (such as ferric phosphate in the case of ferrous metal phosphating) precipitate out of solution and thereby decrease its effectiveness. In addition, the depletion of metal in the solution causes the activity of the bath to decrease. The bath life, if prolonged, can contribute toward waste reduction since the frequency of process solution dumping decreases. The bath life can be increased by periodic or continuous filtering of the bath, regeneration of the spent bath solution, and preventive measures against bath contamination. As the insoluble metallic salts precipitate onto the cooling/heating coils and the object, the effectiveness of the bath goes down. By periodically filtering the process solution, its activity can be maintained (Durney 1984, Saubestre 1957). This is already practiced at many metal finishing operations, especially those with chemical conversion coatings.

  Removal of the soluble salts formed during the treatment process can also extend bath life. The soluble metallic salts that form during the treatment process accumulate in the bath and reduce its effectiveness. These salts

can sometimes be removed by temporarily lowering the bath temperature so as to form solid crystals. In the case of electroless nickel plating, the sodium sulfate that forms can be crystallized by lowering the bath temperature to 41-50°F (Durney 1984). The crystals can then be removed by filtration.

Another process, patented by the U.S. Army, involves the removal of sodium carbonate from sodium cyanide-based plating baths by cooling. Dry ice is used to cool the plating bath, thereby causing the precipitation of the carbonates. The plating solution, free of carbonates, can then be reused. So far, this method has not found widespread use (Arienti 1985, Versar 1985).

Use of an electrolytic diaphragm cell for regenerating spent chromic acid used in etching operations has been reported (AESI 1981). The process uses electrolytic diaphragm cell to oxidize trivalent chromium to hexavalent chromium and remove contaminants. The quality of the regenerated etchant was reported to be equal to or better than fresh etchant. This process, which was still in the developmental stage, would have a great potential for reducing spent chromic acid waste. In one such application, extensively tested at the U.S. Bureau of Mines in Rolla, Mo., copper etching solution was regenerated and metallic copper recovered at the same time. Recovery was accomplished by depositing the copper onto the cathode of the electrolytic diaphragm cell (Basta 1983).

Other measures that can extend bath life are to use automatic control systems, maintain all rack and barrel systems, and practice good housekeeping at all times. Automatic control devices can be used to maintain the concentration by conductivity measurement. A significant change in conductivity would initiate pumping of fresh concentrate into the tank. This type of automatic control is used by large facilities especially for chromate conversion coating (Durney 1984). If the racks or barrels (used for transferring objects to be coated) do not have proper protective coatings, the bath could become contaminated. The process solution can attack the weak spots in the racks or barrels, causing the formation of metallic salts in the bath and thereby lower its activity. Fluorocarbon

coatings applied to the racks or barrels have been found to be effective in minimizing such contamination (Lane 1985). Such a coating will also be helpful in lowering dragout since less bath solution that remains in the corroded crevices on the racks or barrels. Special measures that constitute good operating practices are discussed at the end of this section.

- Metal/acid recovery from spent bath solutions.
  By using electrolysis on the spent bath solutions, useful metals can be recovered and at the same time the hazardous nature of the spent bath can be reduced (Lewis 1980, Campbell and Glenn 1982). This method was implemented in one facility by insertion of electrodes directly into the cyanide destruction tank*. However, electrolysis is used only to a limited extent by the industry (USEPA 1982).

  In addition to recovering metals from the spent bath, spent acid can also be recovered and recycled by means of ion-exchange (Basta 1983). Eco-Tec Ltd., in Ontario, Canada, markets an acid purification system that uses a proprietary resin that recovers mineral acids. The metals are recovered in a concentrated (but still dissolved) form. The concentrated metals can than be recovered by electrolytic means. This process is used by Modine Manufacturing, in Trenton, Mo., to treat copper-contaminated sulfuric acid/hydrogen peroxide solution which was used to brighten brass (Basta 1983). Sodium phosphate salts, formed in nickel/copper electroless plating, can be converted into useful hypophosphite salts by using ion exchange resins activated with hypophosphorous acid. The use of ion exchange resins for regeneration, however, suffers from the disadvantage of generating additional wastes such as spent resins and resin regeneration solutions.

  Another nonelectrolytic means of metal reclamation, still in developmental stages, is the use of bacteria (Basta 1983). Here, the microbes form complexes with the metals in solution, creating a biomass. The biomass can then be burned to recover elemental metal. Laboratory studies in this area are in progress at Polbac Corp. (Allentown, Pa.) and the O'Kelly Companies (Tulsa, Ok.).

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* National Association of Metal Finishers 1985: Personal communication

Another new trend is the use of so-called liquid membranes. These membranes are composed of polymeric materials loaded with an ion-carrying solution (Basta 1983). Liquid membranes were used at Bend Research Inc., in Bend, Ore., to remove chromium from rinse waters and spent baths. Here, chromium in the form of dichromate is drawn across the membrane, forming a tertiary amine metal complex. This complex is then broken down on the other side of the membrane with sodium hydroxide solution. Similar experiments are in progress at the Warren Springs Laboratory in Stevenage, England, for treating wastes from printed circuit board manufacturing.

- Spray/brush methods instead of immersion methods.
  The use of spray/brush methods, which use reagents in a more efficient manner, will reduce the total amount of spent reagents generated. However, spray methods are useful only in continuous applications and when the objects are flat or geometrically simple. Brush application methods are also useful only where the geometry of the object and/or the nature of the operation permits it.

- Use of thinner foils in printed circuit boards manufacture.
  Printed circuit boards are made by the controlled dissolution of the metal foil present on a plastic substrate in an etching solution. By using a thinner metal foil on the plastic board, lower amounts of etching solution are needed and more dilute solutions can be used. This will result in less spent bath wastes. Other techniques allowing for reduction in etching solution use are described in the study of printed circuit boards manufacture (B11).

- Alternatives to conventional metal surface treatment techniques.
  In cyaniding, liquid cyanide salts are used to generate nascent carbon and nitrogen that diffuse into the metal surface, causing it to harden. The same result can be achieved when carbon and steel are exposed to ammonia gas. Ammonia decomposes at about 1550°F to produce nascent nitrogen. Combined with carbon, the gas will diffuse into the metal surface. The use of gas phase carbonitriding alleviates the need for a cyanide solution bath. In addition, the quench-rinsing sequence present in the liquid phase carbonitriding (cyaniding) process would also be avoided. Thus, the waste

generated by spent bath solutions can be eliminated totally. Cyaniding, however, does have several advantages over gas carbonitriding (Schneberger 1981). These include more flexible operation illustrated by the ability to simultaneously treat many small batches which require different cycle times, and a higher heating rate. This is important for cases where the time needed for the object to reach the conditioning temperature may be a large fraction of the total cycle time.

Vacuum evaporation methods for coating nickel, aluminum, and other metals have been developed. Here, metals are evaporated at low pressure using an electron beam and the vapor condenses, as a coating, onto the substrate. This method could be a viable alternative to electroless nickel plating, which generates spent bath wastes. However, the vacuum evaporation method has several disadvantages, e.g., it requires relatively expensive equipment which becomes effective only when a large number of substrates are to be coated, and the uniformity of coating thickness is generally very difficult to control.

Chromium and cadmium can be deposited on steel using ion plating methods instead of electrodeposition. Ion plating uses high-energy ions that bombard the depositing metal which evaporates and then condenses on the substrate. In the U.S., this method is used only when other techniques are found inadequate. However, ion plating is in wide use in Japan where it successfully competes with electrodeposition (Durney 1984).

Chemical vapor deposition (where a chemical reaction decomposes the reactant gases to produce the desired coating material which then condenses on the substrate) can be used for almost any coating operation (Durney 1984). However, its use has been limited to the semiconductor industry, and commercial systems for other applications are not available at the present time.

Ion beam processing techniques, still in the development stage, will be an excellent alternative to case-hardening treatments (Anon 1984). Here, a high energy ion beam is used to harden the surface by implanting the ions in the material.

- Use of less toxic solutions.

  Whenever possible, the use of less toxic solutions for metal finishing will lower the hazard of spent solutions. In the case of electroless copper plating, water soluble cyanide compounds of many metals are added to eliminate or minimize the internal stress of the deposit. It was found that polysiloxanes, such as General Electric silicon fluid SF-96, are also effective stress relievers (Durney 1984). By substituting cyanides with polysiloxanes, the hazardous nature of the spent bath solution can be reduced. Use of trivalent chrome instead of hexavalent chrome in chromate conversion coating can eliminate the toxicity of the spent electroplating baths. Though some manufacturers use trivalent chrome*, its use is not growing rapidly because the quality of trivalent chromium coatings is not as good as that of hexavalent coatings in many applications.* Currently, there were at least five companies that offer trivalent systems (Chementator 1982). Trivalent chromium baths can also use lower metal concentrations. One such solution, developed by W. Canning Materials Ltd. in Birmingham, England, uses only 3.5 gms/liter of total chromium compared to the level of 130 gms/ liters used in traditional hexavalent baths.

- More dilute process solutions.

  The use of dilute bath solutions, whenever possible, would also reduce the hazardous nature of the dumped bath. In the case of cyaniding, a typical bath solution composition is 30 percent sodium cyanide, though some facilities use 45, 75, and 92 percent solutions. By using a 30 percent solution instead of a solution of higher concentration, substantial reduction in the cyanide content of the spent bath solution can be achieved. In electroless copper plating for printed circuit board manufacture, dilute solutions have been tried successfully by many manufacturers (USEPA 1981). The use of dilute bath solution could also lower subsequent rinse water requirements and metal dragout into rinsewater.

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* National Association of Metal Finishers 1985: Personal communication.

- Better operating practices.

  By frequent monitoring of the bath activity and regular replenishment of reagents or stabilizers, bath life can be prolonged (Durney 1984). These reagents or stabilizers differ from process to process. Stabilizers such as 2-mercaptobenzothiozole and methanol are found effective in electroless copper plating used for manufacturing printed circuit boards. The addition of stabilizers can sometimes decrease the deposition rate, but can still be economical in the long run.

  Good control of the bath temperature is important from the viewpoint of performance predictability and is another method of prolonging bath life. Many of the surface treatment operations use tanks with immersed cooling/heating coils. As the salts precipitate and form scales on the coils, the heat transfer is impeded and temperature control becomes increasingly difficult. The heat transfer efficiency can be maintained by periodic cleaning of the coils or by using jacketed tanks instead of coils.

  Proper storage of the process solutions can also reduce waste generation. Usually, the process solutions are stored as a two-part solution and are mixed when a batch is needed. Prolonged storage of these solutions may allow some chemical reactions to occur that could generate contaminants that reduce bath life. In electroless copper plating, if formaldehyde (using as a reducing agent) is stored with a hydroxide, the hydroxide can cause the formaldehyde to breakdown into formic acid and methyl alcohol. Thus, it is better to only store non-reactive mixtures of materials or to store each item separately.

9.1.2 Waste Rinse Water

At the end of surface treatment, objects are rinsed with water, alkali, or acid to remove reagents adhering to the surface or trapped in the crevices of the object. This rinsing may be repeated several times, and the rinse water represents about 90 percent

of the total waste volume gererated (AESI 1981). This stream, containing cyanides and cyanide complexes along with other metal complexes, is treated for cyanide destruction and discharged to the sewer. The following source control methods are suggested:

- Reduction of drag-out.

  In an immersion-type treatment process, small objects are placed inside barrels and bigger objects are supported on racks for immersion into the bath. When the object is removed from the bath, the rack or barrel (and object) carry some reagents with it, called "drag-out". Methods that can be used to reduce drag-out and subsequently lower rinse water requirements are: proper racking of the parts; keeping the racks free of metal buildup and corrosion; increasing drainage time above the process tank; using stationary recovery rinses by installing save rinse or drip rinse tanks; using air blowoff or tumbling to ensure drainage; and using drainage agents (Cheremisinoff, Peina, and Ciancia 1976, AESI 1981, and Cook et. al. 1984).

- Effective rinsing methods.

  By using an efficent rinsing sequence, the quantity of rinse water required can be reduced substantially. Rinsing efficiency can be improved by using properly designed rinse tanks, using air agitation in the rinse tanks, using fog sprays, using automatic valves that control flow rates based on the movement of parts through the processing line, and by using counter-current rinsing (Cheremisinoff, Peina, and Ciancia 1976, AESI 1981, and USC 1983).

  An estimated 90 percent reduction in rinse water can be achieved by using a countercurrent rinse instead of a single running rinse (AESI 1981). Converting to a countercurrent rinse requires only the addition of one or more tanks, appropriate plumbing, and an air agitation system. Because of space limitations or the use of preprogrammed hoist lines, installation of an additional rinse tank may not be possible at many job shops. However, many facilities have reported substantial savings by converting to countercurrent rinsing.

The use of flow control valves can reduce rinse water use by 50 percent with minimal capital costs (AESI 1981). In many instances, excess water is used indiscriminately to ensure total rinse to protect product quality. Though many facilities have installed flow control valves, concerns about reduced product quality have contributed to opposition to such measures (AESI 1981).

Fog sprays, though efficient, are not suitable for all applications. In instances where the coating has little strength initially (as in the case of chromate coatings), fog sprays are generally not used. Use of air agitation in the rinse tanks promotes turbulence in the tank which increases the rinsing efficiency. The use of air agitation in tanks is fairly widespread (AESI 1981).

- Use of immiscible rinses.

  The use of non-aqueous immiscible solvent for rinsing would allow the rinsed solution to either sink or rise during decantation, and the solution could then be returned to the surface treatment bath for reuse without any pretreatment. The rinsing solvent could also be recycled. This process, if feasible, could reduce or eliminate rinse water wastes. Tests with five solvents for use in the chromating process were conducted at the United Technologies Research Center (AESI 1981). A major disadvantage of this method would be the potential for increased air emissions and the need to dispose of spent solvent.

- The use of no-rinse coating processes.

  As the name suggests, no-rinse coatings do not require rinsing after a coating is formed and dried, as there are no residuals left to interfere with the subsequent treatment. Recent developments in chromate conversion coating for the coil coating industry have resulted in a solution that can be applied to steel, galvanized steel, or aluminum, without the need for any subsequent rinsing (USEPA 1982). After the coating is formed, it is dried in air at about 150°F. This no-rinse process, though used by only a few coil coating facilities, can be used for other coating applications (USEPA 1982).

The no-rinse process does have some disadvantages. These are: the inherent high speed of operation requires very efficient control; existing facilities are difficult and expensive to adapt to no-rinse coating operations; and the no-rinse conversion coatings are not FDA approved for food grade coatings.

o Reuse/recycle of rinse water.

A literature review on the reuse and recycle of process water in the metal finishing industry was conducted (Mathews 1980). The following paragraphs deal with some of the reuse/recycle options that are already in use or were suggested for use.

In the chromate process, the first rinse (high in chromic acid), can be recycled to the chromating tank (UNECE 1982). The last rinse can be regenerated using ion-exchange resins and can then be recycled to the rinsing process. Or, by sending the rinse water to an evaporator, the concentrate from the evaporator can be recycled to the coating bath, and the overhead from the evaporator can be condensed and used for rinsing (AESI 1981, Basta 1984). This scheme (illustrated in Figure 9-1) can reduce rinse water requirements drastically. The method requires sufficient water to be evaporated and recycled to satisfy rinsing requirements. The economics of such systems has been discussed in detail elsewhere (AESI 1981). Case studies of facilities using evaporators have also been reported (Lewis 1980). The use of atmospheric evaporators, while decreasing energy requirements, requires significantly more floor space than conventional evaporators. Such systems are in use at some facilities (Campbell and Glenn 1982).

Concentration of rinse water for recycle to plating baths or for reuse can be achieved using ion exchange resins. A reciprocating flow ion exchanger for drag-out recovery from chromium, copper, and mixed coating processes is in current usage. The use of similar ion exchange columns for rinse water treatment and reuse is expected to have great potential in the future. The use of ion exchange columns does have some disadvantages. These are: ion exchange is more expensive than conventional chemical

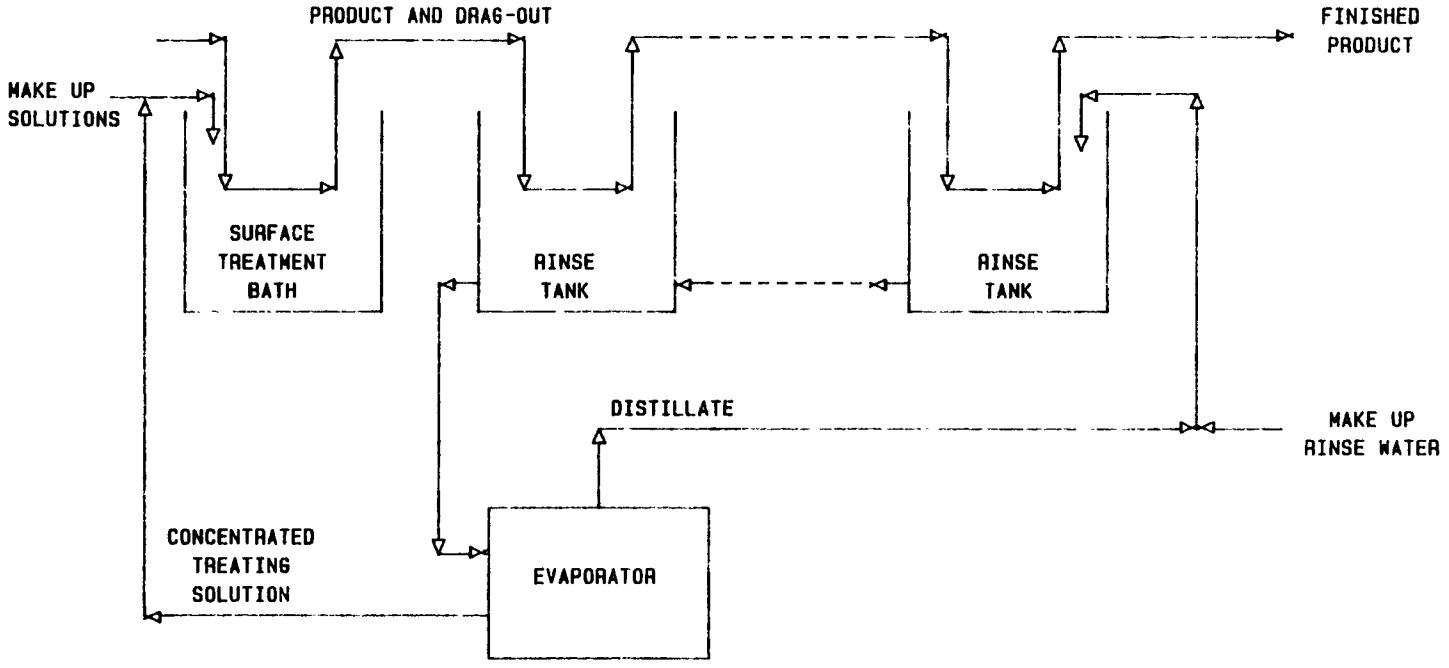

Figure 9-1 Closed Loop Evaporation System for Metal Surface Treatment Waste Reduction

treatment; regeneration steps generate their own wastes; and the process is only favorable for streams with a low concentration of contaminants (up to approximately 250 ppm).

Reverse osmosis for concentrating rinse waters has found limited use. Here, water is preferentially forced through the pores of a semi-permeable membrane and two streams are generated: a concentrated salt solution that can be sent to the bath, and a pure water stream that can be used for rinsing. Some of the limitations confronting the process are that the membranes operate in the high pH range only (pretreatment to assure high pH is necessary); the reliability or durability of the membranes under variable conditions characteristic of mixed wastewater is questionable; supplemental evaporation (to boost concentration) may be necessary before the salt solution can be recycled to the coating process; and the process is economical only for processes with high drag-out rates (something that can be controlled by good operating practices). Cellulose acetate membranes are used by some nickel coating facilities. Other potential membrane applications include copper, zinc coating, and chromating operations.

The electrodialysis process uses alternately placed anion and cation permeable membranes and separates the rinse waters into a dilute stream that can be used for rinsing and into a concentrated stream that can be recycled to the coating operation. The process is continuous and the major operating cost is for electricity. Currently, some nickel, zinc, and chromating facilities use this process.

- Replacing hexavalent chromium with trivalent chromium.
  In chromate conversion coatings, hexavalent chromium can be replaced by trivalent chromium, which reduces the hazardous nature of rinse waters. This method is discussed in more detail in Section 9.1.1.

- Replace cyaniding by gas carbonitriding.
  As explained in Section 9.1.1, cyaniding requires a quench-rinse operation to wash cyanides present on the objects. The use of gas carbonitriding eliminates the need for this rinsing operation that generates a hazardous waste stream.

- Use of still rinsing.

  The work piece can be immersed in a still rinse tank following the metal finishing bath. The still rinse tank has no inflow or outflow of rinse water, and the finishing bath constituents build up in it. When the rinse water in the still rinse tank becomes concentrated enough, it can be used to replenish the finishing bath solution. The use of still rinsing can cut down the quantity of rinse water required. This process, when used for initial rinsing, can facilitate metal recovery from the rinse water. Still rinsing is usually followed by a spray or countercurrent rinse to ensure the complete removal of contaminants.

- Metal reclamation from rinse water wastes.

  By using electrolytic or non-electrolytic methods, as explained in Section 9.1.1, metals present in the rinse waters can be recovered. This reduces the hazardous nature of this stream.

- Changing rinse composition.

  Changing the rinse composition to reduce its hazardous nature should be attempted whenever possible. In a zinc-based phosphating bath, the final rinsing of the object is usually done with dilute chromic acid. Environmental concerns about chrome caused several facilities to develop and use chrome-free rinses, even though these rinses were not as effective as the chrome-containing rinses (Schneberger 1981).

- Minimizing process water use.

  By reusing rinse water effluents from certain operations in other operations with lower rinse water quality requirements, overall aqueous wastes can be minimized. The use of water from fume scrubbers has been shown to be practical for rinsing in certain cases (Cheremisinoff, Peina, and Ciancia 1976). Used cooling water or steam condensate might also be used for rinsing if technically permissible and economically justified.

- Better operating practices.

  A typical metal finishing facility has various coating operations being performed at the same time, and mixing of various rinse streams is not

uncommon. By segregating various rinses, their reuse or recycle can be promoted. Metal reclamation by electrolysis from these various streams is easier if they are not mixed together. In the recent past, rinse waters and spent baths were mixed and treated together. Segregating spent bath wastes from rinse water wastes is quite common at present.

9.1.3 Solid Wastes

Solid wastes are generated during the filtration of the bath to remove precipitated metallic salts, and by the clarification, dewatering, and filtering operations performed during waste treatment. These solid wastes are usually disposed of by landfilling or are sent to an outside reclaimer. The following source reduction techniques are considered:

- Metal reclamation from the solid waste.
  It was reported by Lisanti and Helwick (AESI 1981) that a certain facility hauled solids to another plant within its corporation for metal reclamation. Depending on waste volume, such recovery can be an uneconomical proposition in terms of capital costs. Individually, the quantities generated might not be large enough to justify a dedicated recovery system. The alternative to individual treatment systems for metal recovery would be a centralized waste treatment facility, where the wastes could be collectively treated. In such a facility, the recovery options would be more economically attractive. Such centralized treatment facilities are in operation in West Germany.

- Effective dewatering of the solids.
  Solids are dewatered by some facilities using a filter press. By effectively dewatering the solids, the quantity of waste sent for landfilling can be decreased by about 50 percent (AESI 1981). More effective dewatering can be achieved using disc, scroll, or basket type centrifuges, vacuum drums or belt filters.

9.1.4 Spills and Leaks

Spills are the result of overflow from various process tanks and other inadvertent discharges, such as valve closure failure, leaky gaskets, and drips. The following source reduction method is postulated:

- Better operating practices.
  By using splash guards and drip boards, spilled liquids can be recycled and spilled cleaning wastes can be avoided. Use of float valves or alarm systems are inexpensive options to prevent overflows. Other possibilities include liquid level controllers. Good housekeeping measures such as periodic inspection of process equipment and piping, periodic relining of the tanks, and training and educating personnel to be cognizant of the importance of controlling waste generation can reduce the number and size of spills and leaks occuring in a facility.

9.1.5 Stripping Wastes

Stripping wastes, which are generated most commonly in small job shops, are the result of removing old or bad coatings on objects prior to the required surface finishing operation. The operation is essentially an etching type treatment, whereby the coating is dissolved in an acid. Since the same bath may be used to strip various metal objects, this waste is difficult to deal with since recycling or regeneration is not generally possible. The following source reduction techniques are suggested:

- Use of non-chrome etchants.
  Whenever possible, ferric chloride, or ammonium persulfate solutions should be used instead of chromic-sulfuric acid etchants. However, compatibility with the planned surface treatment must be carefully examined. The use of such etchants will reduce the toxicity of the stripping solution that ends up as a waste.

- Decrease the generation of off-spec coatings that require stripping.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE METAL SURFACE TREATMENT INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Spent Bath Solutions (*)	1 Extend bath life	2	2	1	1	2		0 3	0 4	
	2 Metal/acid recovery from spent baths	1	2	2	1	2		0 5	0.8	0.8
	3. Spray/brush items instead of immerse	1	1	1	2	1		0 5	0.1	
	4. Use thinner foil for P.C.B.'s	1	1	2	3	1		1.5	0 1	
	5 Alternative treatment techniques	2	2	2	1	1		0.5	0.4	
	6 Use of less toxic solutions	1	2	2	2	2		1.0	0.5	
	7. More dilute process solutions	1	2	2	1	2		0.5	0.8	0.8
	8. Better operating practices	1	2	2	2	3		1.0	0.8	0 8
	Overall	1.25	1.75	1.75	1.63	1.75	0.15	1 5	0.5	0.8
Waste Rinse Water	1. Reduce dragout of solution from tank	2	2	2	1	3		0.5	1.1	
	2 Employ effective rinsing methods	2	2	3	1	3		0.8	1.7	1.7
	3 Use of immiscible rinses	1	2	1	0	1		0 0	0 3	
	4. Use of no-rinse coatings	1	2	3	1	2		0 8	1 1	
	5 Reuse and recycle spent rinse water	1	2	2	2	3		1.0	0.8	
	6. Replace hex chrome with trivalent	1	2	2	1	1		0.5	0.4	
	7. Replace cyaniding with gas carbon.	1	1	3	1	1		0.8	0.6	
	8. Use still rinsing technique	1	1	2	1	2		0.5	0 8	
	9. Reclaim metal from rinse water wastes	3	3	2	2	2		1.0	0 5	
	10.Change rinse composition	1	2	2	1	1		0 5	0.4	
	11.Minimize process water use	1	2	2	1	2		0.5	0 8	
	12.Better operating practices	1	2	2	1	2		0.5	0.8	
	Overall	1.33	1 92	2 17	1 08	1.92	0.65	1.0	0.8	1.7
Filter Wastes (*)	1. Metal reclamation from solid waste	1	1	2	1	1		0.5	0 4	
	2. Effective dewatering of the solids	1	2	2	1	2		0.5	0.8	0 8
	Overall	1.00	1.50	2.00	1.00	1.50	0.05	0.5	0.6	0 8
Spills and Leaks	1. Better operating practices	2	1	2	2	2		1.0	0.5	0 5
	Overall	2 00	1 00	2 00	2.00	2.00	0 05	1.0	0.5	0 5
Stripping Waste	1. Use of non-chrome etchants	1	1	2	1	2		0 5	0.8	0 8
	2. Reduce generation of off-spec coating	1	1	2	1	2		0 5	0.8	0 8
	Overall	1 00	1 00	2 00	1 00	2.00	0 10	0 5	0 8	0 8
All Sources	All Methods						1 00	1 0	0 7	1 3

(*) These streams included listed "F" and/or "K" RCRA wastes

9.2 Implementation Profile

The source control methods discussed for use by the metal surface finishing industry have different potentials for application depending on whether the facility is a captive shop or a job shop. Job shops are usually required by their clientele to follow certain operating procedures, and most job shops buy their process solutions from manufacturers. Thus, modifications in certain operating procedures and changes in process solutions are not feasible in many job shops without the guidance and approval of the customer. Also, because smaller operations usually have space limitations, installation of additional tanks for countercurrent rinsing may not be practical. For facilities which have preprogrammed hoist lines in operation, changes in operations such as rinsing may be difficult. However, measures such as the installation of flow control valves, splash guards, etc., which do not require much capital or space can be used by all facilities. Efficient use of water can be made by reusing spent process water at places that require low quality water. Improvements in operating practices, such as spill and leak prevention, are additional measures which require little capital to implement.

Reclamation of metals from wastes is an effective way to reduce or eliminate the hazardous constituents of these wastes. In many job shops, the volume of wastes may be too low for economical recovery of metals. In such cases, the use of centralized waste treatment facilities to collect and treat wastes from various plants has proven in some to be a long-term economical solution.

9.3 Summary

The summary of all noted source control techniques is given in Table 9-1. Each technique was rated for its effectiveness, extent of current use and future application potential on scale of 0 to 4. The ratings were derived by project staff based on review of the available data and in consultation with the industry. The estimates of current level of waste reduction achieved (current reduction index) and possible future reduction (future reduction index) were obtained from the ratings in accordance with the methodology presented in the introduction to this appendix.

The current reduction index (CRI) is a measure of reduction of waste that would be generated if none of the methods listed were implemented to their current level of application. For the entire metal surface finishing industry, CRI is 1.0 (25 percent) which is indicative of the low to moderate level of waste minimization that already has taken place. Current measures that have proven effective as a whole have been the use of less toxic bath solutions, the reuse and recycling of spent rinse water, the reclaiming of metal from waste, and the implementation of better operating practices.

The future reduction index (FRI) is an indication of the level to which the currently generated waste can be reduced if all of the techniques noted were implemented according to their rated potential. The FRI value of 0.7 to 1.3 (18 to 33 percent) is indicative of the moderate extent of future waste reductions. Among the techniques that were found most effective and applicable (as evidenced by high FRI value), employment of effective rinsing methods, metal/acid recovery from spent baths, use of more dilute process solutions, and further implementation of better operating practices appear to promise the greatest level of reduction for the industry as a whole.

10. PRODUCT SUBSTITUTION ALTERNATIVES

Since many metal objects can be coated with several alternative metals to achieve the same quality of treated surface, certain substitutions could contribute towards hazardous waste reduction. The replacement of nickel by zinc is possible in some instances. In other applications, zinc can be substituted by manganese or iron. Electroless nickel plating, used by some printed circuit boards manufacturers, can be substituted with electroless copper plating. Cadmium and silver can generally be substituted with other metals.

11. CONCLUSIONS

The estimates indicate that moderate reductions of waste generated by the metal surface finishing industry are possible, probably in the 18 to 33 percent range. Several effective source control measures include use of efficient rinsing techniques, recovering metal/acid from spent baths, use of more dilute process solutions and further implementation of better operating practices.

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13. INDUSTRY CONTACTS

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W.G. Vaux, P.E., Chemical and Process Engineering, Westinghouse Electric Corp., Pittsburgh, PA.

1. PROCESS: ORGANIC DYES AND PIGMENTS MANUFACTURE

2. SIC CODE: 28652, 28653

3. INDUSTRY DESCRIPTION

Manufacturers of organic dyes and pigments are included as part of the cyclic crudes and intermediates manufacturing industry. The companies are engaged in the conversion of cyclic organic chemicals into more complex intermediates, and/or in the subsequent formulations of these products into dyes and pigments.

3.1 Company Size Distribution

The 1982 Census of Manufacturers (USDC 1985) reported a total of 143 companies involved in the manufacturing of cyclic crudes and intermediates, with 189 manufacturing plants located throughout the U.S. As of 1983, 22 companies produced only dyes, 21 produced only pigments, and 12 produced both dyes and pigments. Since no specific size data were found for the organic dyes and pigments sector, Table 3-1 gives the company size distribution in terms of the number of employees for the entire cyclic crudes and intermediates manufacturing industry.

Table 3-1 Company Size Distribution

	No. of Employees Per Facility						
	Total	1-49	50-99	100-249	250-499	500-999	1000-2500
No. of establishments	189	93	25	41	18	8	4
No. of employees	27,075	2,325	1,875	7,175	2,700	6,000	7,000

Source: 1982 Census of Manufacturers (USDC 1985).

3.2 Principal Producers

The principal producers of organic dyes and pigments are listed below:

Mobay Chemical Corporation
Sandoz Chemicals Corporation
Toms River Chemical Corporation
ICI United States, Inc.
Crompton & Knowles Corporation
Atlantic Industries, Inc.
BASF Wyandotte Pigments
Sun Chemical Corporation
American Hoechst Corporation
Harshaw-Filtrol Partnership
Galaxie Chemical Corporation
Ciba-Geigy Corporation

3.3 Geographical Distribution

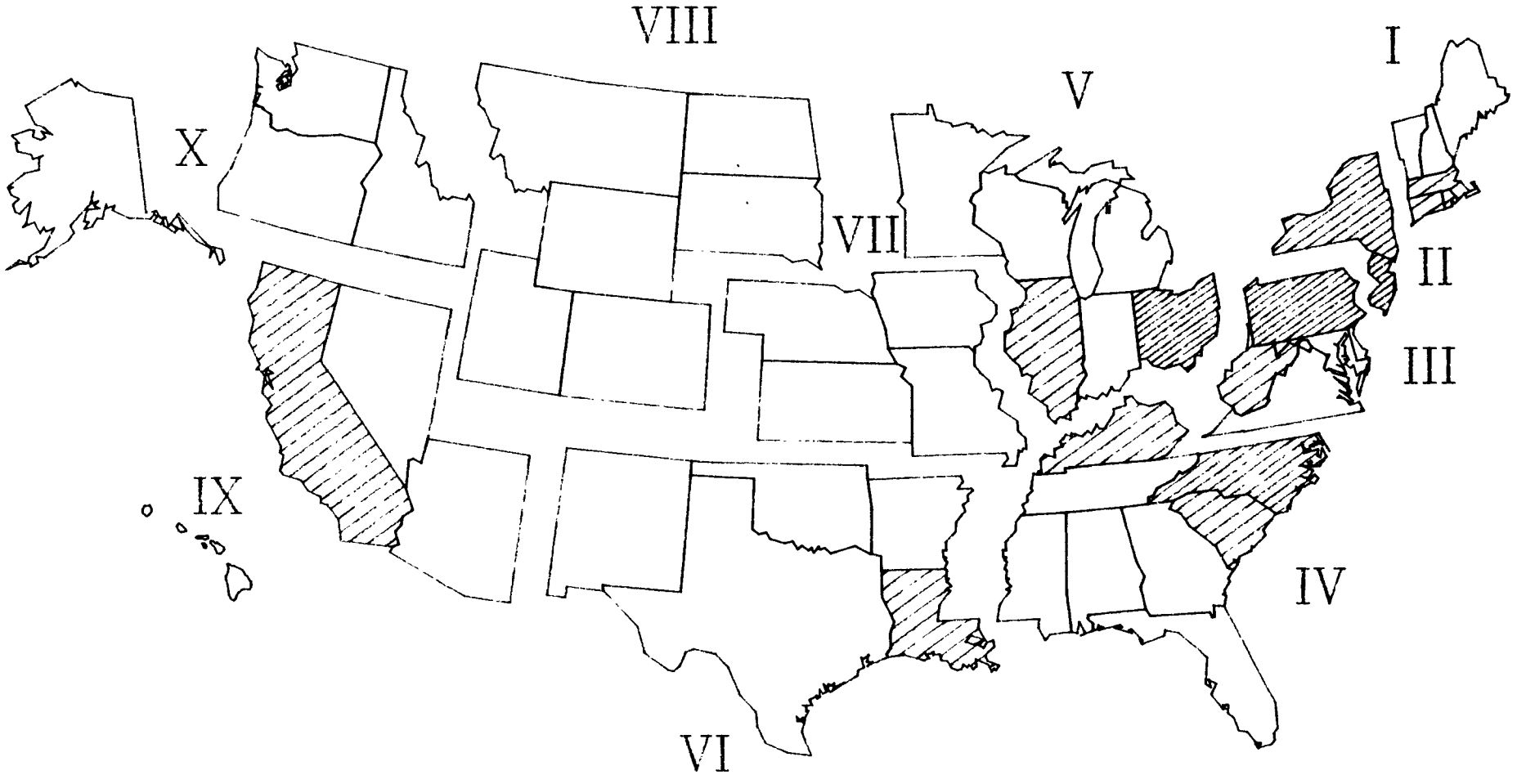
According to data from 1977, there were 55 companies producing organic dyes and pigments at 87 manufacturing sites. Among these, 89 percent of the plants were located in 11 eastern states. The remaining sites were distributed throughout the country as shown in Figure 3-1 and Table 3-2 below:

Table 3-2 Location of Organic Dyes and Pigments Manufacturing Facilities in th U.S.

EPA Region	No. of Establishments
I	8
II	38
III	11
IV	13
V	12
VI	0
VII	1
VIII	0
IX	3
X	0
National	86

Source: Industrial Process Profiles (Radian Corp., 1977).

(a) The location of one plant was not reported.



Roman numerals show EPA regions

Figure 3-1 Organic Dye/Pigment Plants in the U.S.

4. PRODUCTS AND THEIR USE

There are over 1000 different dyes and pigments being produced in the U.S., with pigments being fewer in number (approximately 10 percent). These products are sold as pastes, powders, lumps, dispersions in organics, or aqueous solutions with concentrations between 6% and 100%. Of the total quantity of dyes produced, two-thirds is used as colorants in the textile industry, one-sixth is used in coloring paper, and the rest is used in producing organic pigments and in the dyeing of leathers and plastics. For pigments, one-half of the quantity produced is used in printing, while the rest is used as colorant for paints, plastics, textiles, and paper.

According to their applications, dye products are classified into 10 principal classes. These are: (1) acid dyes, (2) basic dyes, (3) direct dyes, (4) disperse dyes, (5) reactive dyes, (6) fluorescent brightening agents, (7) food, drug and cosmetic colorants, (8) mordant dyes, (9) solvent dyes, and (10) vat dyes. U.S. annual production of dyes in 1983 was 122 thousand short tons per year (TPY) (USITC 1983). The production of direct and solvent dyes decreased as compared to the previous years, while the production of the remaining 8 classes increased. Fluorescent brightening agents accounted for the largest portion of dyes produced in 1983 (25%). For the remaining classes, vat dyes, disperse dyes, direct dyes, and acid dyes accounted for 21%, 15%, 12%, and 11% of the annual total production, respectively.

Pigments are classified either as toners or lakes. Toners are full-strength organic or metallo-organic colorants that do not contain any inorganic pigments or carriers. Lakes, on the other hand, are combinations of a dye with an inorganic carrier, usually alumina hydrate. The production rate of pigments in 1983 was 39 thousand tons per year, with 99% of the amount produced as toners (USITC 1983).

5. RAW MATERIALS

A wide variety of organic and inorganic materials are used in the production of organic dyes and pigments. Large manufacturing plants produce their own dye intermediates from basic units such as benzene or naphthalene. Small manufacturers, however, will bring in intermediates from other sources, often foreign. Most of the organic intermediates are hazardous in nature, with some being identified as carcinogenic.

The common types of raw materials used in this industry are listed below (Catino and Farris 1979, Bannister, Olin, and Stingle 1979, Fytelson 1982, Radian 1977, SRI 1984):

Organics: derivatives of benzene, toluene, naphthalene, anthraquinone, and other aryl systems including heterocyclics, which contain functional groups such as sulfonic acid substituents, hydroxyl, amino, alkylamino, chloro, nitro, carboxyl, alkoxyl and others; reagents such as lower alcohols and amines, formaldehyde, phosgene, dimethylsulfate, acetic acid, and glycerine.

Inorganics: alumina hydrate, aluminum salts, ammonium salts, calcium chloride, sulfur, chlorine, bromine, chromium salts, copper and copper salts, iron and iron salts, iodine, nickel salts, sodium salts, potassium salts, lead peroxide, phosphorous chlorides.

Acids: sulfuric acid, oleum, nitric acid, hydrochloric acid, chlorosulfonic acid, acetic acid, chloroacetic acid.

Bases: ammonia, calcium carbonate, sodium hydroxide, calcium oxide.

Catalysts: zinc chloride, aluminum chloride, ferric chloride, iron, Raney nickel catalyst, stannous chloride, magnesium oxide, manganese dioxide, lead peroxide.

6. PROCESS DESCRIPTION

Organic dyes and pigments are produced from a great variety of cyclic intermediates using many processes. Manufacturers often purchase organic chemicals, usually in the form of cyclic benzenoids, and convert these into more complex intermediates, and ultimately into dyes and pigments. The distinction between dyes and dye intermediates is somewhat arbitrary, since some dye intermediates may be used as dyes, or they can be further processed to form other dyes or pigments. Similarly, pigments are differentiated from dyes based on application methods rather than chemical constitution. Pigments are much less soluble and they retain their granular form throughout the application process.

Although the number of different types of organic dyes and pigments produced is large, the majority of these products can be classified into eight basic classes which are based on the chemical structure of the common color-bearing units (chromophores) in the molecules. These include:

- o azo dyes and pigments,
- o anthraquinone dyes and pigments,
- o stilbene dyes and fluorescent brightening agents,
- o diphenyl methane and triarylmethane dyes and pigments,
- o methine and polymethine dyes and pigments,
- o xanthene dyes and pigments,
- o phthalocyanine dyes and pigments,
- o sulfur dyes.

Of the eight classes, azo dyes and pigments represent the most important class commercially produced in the U.S., accounting for 35 percent of all U.S. dye and pigment production in 1978. Since data on U.S. production by structural class have not been reported since 1978, the information on present relative and total production of these dyes and pigments, by class, remains uncertain. Nevertheless, based on the information provided in a recent EPA report on the waste generation from the organic dyes and pigment industry (SRI 1984), it is believed that azo dyes and pigments still represent the largest volume of dyes and pigments produced. Therefore, this report will focus on the production of azo dyes and pigments. Their manufacturing process will be examined in detail to exemplify the degree of complexity which can be encountered in the production of organic dyes or pigments.

Figure 6-1 presents the flow chart for the manufacturing of azo dyes and pigments. There are basically three general stages in the production of any dye or pigment. These are:

- Synthesis stage.
  Operations performed in this stage vary widely among the dyes and pigments due to the differences in the sequence of reactions required to obtain the desired structure of a specific dye or dye intermediate.

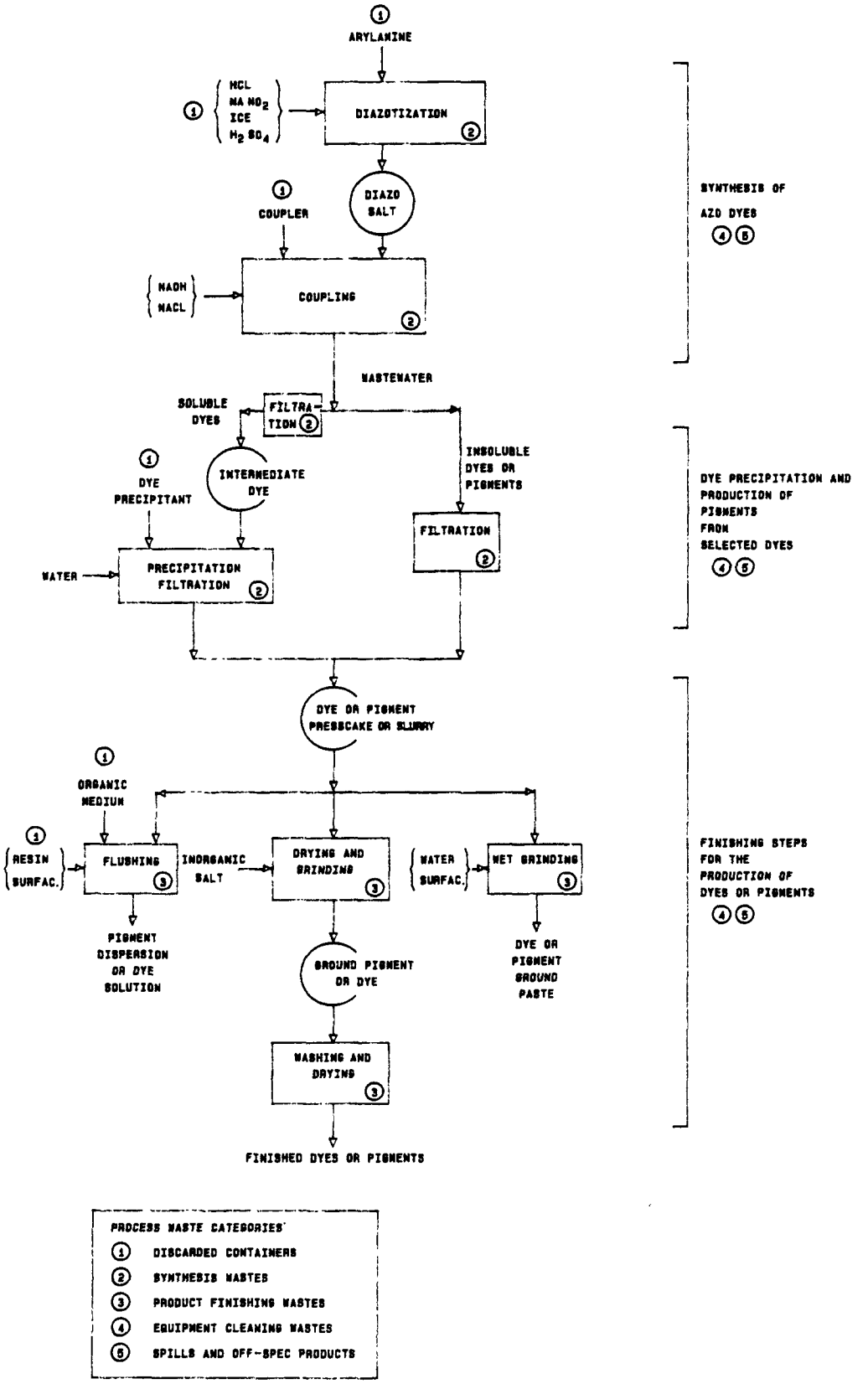


Figure 6-1 Block Flow Diagram for the Production of Azo Dyes and Pigments

- Precipitation stage.
  Dyes which are still soluble after the last of the reaction sequence are often precipitated out by the addition of salts. Similarly, pigments can be obtained directly or from the precipitation of dye intermediates on resin, or by the addition of metal salts.

- Finishing stage.
  This stage is common to the production of all dyes and pigments. It usually involves the processing of dyes and pigments into their final forms through operations such as drying, grinding and standardizing as required by the dye users.

The following sections describe in detail the steps involved in each of the stages for the production of azo dyes and pigments.

6.1 Synthesis of Azo Dyes and Pigments

Azo dyes are compounds containing one or more azo groups (-N=N-) in their molecules. Azo dye products consist of direct dyes, acid dyes, pigments, and a small amount of azoic compounds which are incomplete dyes that require coupling during the application process. Azo dyes and pigments are produced via a two-step process consisting of the diazotization and coupling of aromatic amines.

The manufacturing process begins with a diazotization reaction. In this first stage, arylamines such as anilene are reacted with nitrous acid to form diazonium chloride salt according to the reaction:

$$ArNH_2 + NaNO_2 + 2HCl \dashrightarrow ArN = N^+Cl^- + NaCl + 2H_2O$$

where Ar is an aromatic group. Since nitrous acid is very unstable, it is produced as needed from the reaction of an aqueous solution of sodium nitrite and hydrochloric acid. The batch reaction is carried out at 32°F - 40°F in a period of 1-3 hours using arylamine, $NaNO_2$, and HCl in a molar ratio of 1:2:3.

The product is an aqueous solution containing 15% diazonium chloride and 7% NaCl. In the production of azo dyes, as well as of any other dyes and pigments, the reactions

are almost always carried out in batch reactors because the small total demand does not justify the use of a continuous process. The reactions are carried out batchwise in one or several reactor trains. Each train includes at least one diazotizing reactor, one coupling reactor, and one filter press. The kettles are made from cast iron, stainless steel, glass-lined steel, wood, or brick, and have a capacity of 500 to 10,000 gallons. The reactors are equipped with mechanical agitators, temperature recorders, and pH-probes. Jackets or coils are used for heating and cooling. Unjacketed reactors are also used, and the temperature is controlled by direct introduction of steam or ice.

The yield from a diazotization reaction is fairly high. The use of HCl, however, may result in the formation of byproducts. For example, the diazonium salt may decompose into compounds which may be further chlorinated into polychlorinated organic byproducts. Furthermore, the decomposition products may react with the original arylamine to form secondary amine compounds. These secondary amine compounds can then react with nitric acid and form insoluble compounds.

A clarification operation is often performed to remove these solid by-products before the intermediate is transferred to the coupling reactor. The resulting solid waste is often sent to land disposal. In addition to these byproducts, other major contaminants include undecomposed diazotic acids. Once clarified, the intermediates from the diazotization reactor are then transferred to the coupling reactor.

In the second stage where coupling occurs, the diazonium salt is reacted with another aromatic compound, called a "coupling component," which has a strong electron-donating substituent such as a phenolic, amino, or substituted amino functional group. The reaction forms azo compounds in the following manner:

$$Ar\text{-}N{=}N^{+}Cl^{-} + Ar'\text{-}H \longrightarrow Ar\text{-}N{=}N\text{-}Ar' + HCl.$$

Coupling is generally conducted in a mildly alkaline condition by the addition of NaOH. The reactor is operated at $32^{o}F$-$40^{o}F$ for 4-24 hours. The ratio of diazo salt to the coupling component varies depending on the degree of coupling required. High pH is often avoided so as to minimize non-coupling reactions leading to the formation of undesirable byproducts, e.g. triazene compounds:

$$ArN_2 + Cl^{-} + Ar'NH_2 \xrightarrow{NaOH} Ar\text{-}N{=}N\text{-}\underset{H}{N}\text{-}Ar' + H_2O + NaCl$$

Furthermore, coupling reactions must compete with the decomposition of the diazonium salts to form phenols as byproducts from the reaction:

$$ArN{=}N^{+}Cl^{-} \rightarrow N_2 + (Ar^{+}Cl^{-}) \xrightarrow{NaOH} ArOH{+}NaCl$$

In addition, undecomposed diazotic acids carried over from the diazotization reactor may react in the basic medium to form diazotate salts. These salts are insoluble and often require filtration of the coupling reactor effluent to remove them from the soluble dye solution. The resulting filter press cake is sent to land disposal.

6.2 Soluble Dye Precipitation and/or Pigment Production from Selected Dyes

Dyes formed from the coupling reaction, or formed at the end of the synthesis sequence in general, can be either soluble or insoluble. Insoluble dyes (or pigments) are often filtered, and the products are collected in the form of filter press cakes. These are then sent to dye/pigment finishing operations before being sold as final products. Soluble dyes are precipitated by the addition of salts. The resulting slurry is filtered, and the press cake is air blown to remove the mother liquor. The dyes are then transferred to finishing steps. The mother liquor which contains byproducts and residual dyes and pigments is treated on-site with other process wastewaters before being discharged. Similarly, dyes that are too easily soluble in water and/or organic solvents can be converted into pigments with the requisite low solubility characteristics. These pigments (lakes) can be formed by precipitation of water soluble dyes on an adsorptive surface such as resin or alumina hydrate, or from the precipitation of an acid or basic dye using inorganic salts. Lakes formed from acid dyes are precipitated by the addition of soluble salts of alkaline-earth metals, while lakes formed from basic dyes are made from precipitation with regular metal salts. The precipitation process is carried out by stirring dyes and dye precipitants in a steel vat. The reacting solutions are heated to 120°F-170°F, and fed in at a prescribed rate. The product slurry is then cooled to obtain the desired crystalline form of the pigment products. The product slurry is filtered, and the resulting filter press cakes are sent to finishing operations. The mother liquor containing residual dyes, pigments and metal salts is not recovered and is sent to wastewater treatment.

6.3 Finishing Operations

After the dyes or pigments are collected in cake form or as slurries, they are sent through a series of finishing steps before being sold as final products. The physical form of the product plays an important part in the marketing of the material. Pigment attributes such as crystal size, specific, surface, and particle shape have enormous influence on the quality and performance of a pigment.

One important finishing operation is called flushing. This is used to transfer pigments from a water-borne phase to an organic or oil-borne phase (67 percent of pigments are sold in this organic form). The flushing operation is usually done in more than one charge in steel tanks equipped with high speed stirrers or blade agitators. The residual water from these charges is then removed by vacuum stripping. The finished products are pigment dispersions or dye solutions. Resins and surfactants are usually added to stabilize the dispersion. Wastewaters from the flushing operations containing organic chemicals are sent to treatment before being discharged.

Conventional final finishing is accomplished through dry grinding of the product. The crude product press cakes or slurries are dried and then ground. Typically, ball or hammer mills are used. Drying is done in hot air or vacuum using ovens, rotary dryers, drum dryers, or most frequently, spray dryers. The dry grinding process is losing its popularity, however, due to dusting which causes air pollution problem. This operation can be replaced by wet grinding which is done in ball or sand mills. Surfactants are often added to facilitate the grinding process. The resulting product is a ground aqueous paste which can be subsequently dried by spray drying.

The last important finishing step is a standardization step in which inert salts are often added to meet product specifications, which can vary widely. For example, of the total amount of organic pigments sold, 45 percent is sold as dry powder without dilution, 40 percent is sold as colorants in oil with up to 65 percent dilution by inerts, and the remaining 15 percent is sold as wet filter cake without further processing.

7. WASTE DESCRIPTION

The primary specific wastes associated with the organic dyes and pigments manufacturing industry are listed in Table 7-1. Wastes or process residuals from this industry were classified as follows:

Discarded Shipping Containers: Empty containers, paper bags, or fiber drum liners that contain residual amounts of organic intermediates or other raw materials.

Synthesis Wastes: Generally, these include the byproducts of the various reaction steps prior to finishing. The byproducts are formed as a result of undesirable side reactions that occur in series or in parallel to the main reaction leading to the desired product. Synthesis wastes also contain unconverted reactants and coproducts (e.g. salts), all dissolved in the reaction medium such as water or solvent.

As to the form, composition, and the point of exit from the process, synthesis wastes vary. In the case of soluble azo dyes, these wastes exit as a solid cake from filtration following coupling and in liquor following filtration of the precipitated dye. In case of anthraquinone dyes, the synthesis wastes would be present in the distillation column bottoms, which also contain organic solvent.

Considerable variability in the treatment and ultimate disposal of synthesis wastes is expected given the large number of manufacturing facilities. Some plants treat the filter cakes with hypochlorite solution to reduce the amount of organic material prior to land disposal of the left-over solids. The aqueous waste containing residual organic and inorganic compounds can be also treated by oxidation to reduce oxygen demand, color and turbidity to acceptable levels prior to discharge. The alternatives for solvent waste include solvent recovery and/or disposal of residuals via landfilling or incineration.

Product Finishing Wastes: Since equipment cleaning and spill/off-spec product wastes are considered separately, the wastes from the finishing steps include dusts generated during drying and grinding which are collected in the baghouse. Additionally, these wastes would include residual water or organics from the flushing step. Usually, these wastes are minor in comparison to other waste categories noted.

Table 7-1 Organic Dye/Pigment Manufacturing Process Wastes

No.	Waste Description	Process Origin	Composition	RCRA Code
1.	Used containers	Unloading of raw materials	paper bags and fiber drums containing residual amounts intermediates	--
2.	Synthesis wastes	Reaction steps	water, organic solvents, metal salts, intermediates, side reaction byproducts	F002 F003 F004 F005
3.	Product finishing wastes	Product drying, flushing, grinding, standardizing, packaging	dyes, pigments, intermediates, inert salts, auxiliary oils	--
4.	Equipment cleaning wastes	Cleaning of equipment between batches	dilute alkaline or acidic aqueous solutions or solvents with small amounts of residual organics	--
5.	Spills and off-spec products	Cleaning of spills, off-spec product generation	dyes, pigments, organic intermediates.	--

Equipment Cleaning Wastes: These include aqueous and solvent streams associated with the cleaning of reactors, transfer lines and equipment. Cleaning is done between consecutive dissimilar batches in order to prevent contamination. It is expected that in an average facility employing a number of reactors, tanks and filter presses, cleaning is performed using a clean-in-place system employing either flow-over or fill-and-empty techniques. The ball mills and other mechanical equipment used in the finishing operations is expected to be cleaned using fill-and-empty approach.

The cleaning medium can be alkaline aqueous solution or solvent. At times, an oxidizing agent, such as hydrogen peroxide, may be added. The sludge separated from the cleaning solution can be co-mingled with other solid process residuals prior to possible treatment and disposal. The aqueous effluent is neutralized prior to discharge, but can also be mixed with liquid streams from the synthesis step prior to neutralization, treatment and discharge.

Spills and Off-Spec Products: These wastes are generated as a result of inadvertent operation, usually attributable to human error. Again, diversity of chemical species, availability of treatment, and plant operating procedures prevent one from compiling precise information on handling and disposal of these wastes. However, it is expected that a high degree of effort is expended in attempts to recover valuable chemicals from spills or spoiled batches before spill wastes are disposed of as residuals, probably through landfilling.

8. WASTE GENERATION RATES

Recent effort has been made to characterize the waste streams generated from the manufacturing of organic dyes and pigments (SRI 1984). Information about the quantity of these wastes, however, was not in evidence at the time of the final document preparation. The relative proportions of each waste stream were estimated by project staff based on the available information and are given in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

A summary of the waste sources and the corresponding source reduction methods is given in Table 9-1. This section deals with the description of the listed methods, including known application cases.

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" has also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel practices
  - management initiatives
  - employee training
- o Procedural measures
  - documentation
  - material handling and storage
  - material tracking and inventory control
  - scheduling
- o Loss prevention practices
  - spill prevention
  - preventive maintenance
  - emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Containers

Raw materials used in the production of organic dyes and pigments are usually shipped in paper bags or fiber drums. Since some of these materials are toxic in nature, the discarded containers containing residual amounts of these substances can be considered as hazardous. The following source reduction techniques were noted:

- Use rinsable/recycleable drums and plastic liners.
  The use of polyethylene bags to line steel drums is already well established in the industry along with the use of reusable tote bins. The residual use of paper bags or liners should be eliminated.

- Maximize size of container.
  Here, the underlying principle is that the same volume of material has a smaller external surface if supplied in a single container as opposed to a number of smaller containers. As the residual amount depends on the size of the "wetted" surface, less waste residue will result from the use of larger containers. Switching from drums or bags to mega-drums, tote bins and, where possible, to bulk handling has already been accomplished to a significant degree, but a moderate improvement margin probably exists.

- Container segregation.
  Since only the organic intermediates and a few other reagents are hazardous while a large amount of other raw materials, such as inert salts used for dye and pigment standardization operations, are not, separation of the different types of empty disposable containers can greatly reduce the amount of potentially hazardous waste generated from this source.

9.1.2 Synthesis Wastes

In the azo dyes example, synthesis steps include diazotization, coupling and precipitation. In a more general context, the synthesis of all dyes and pigments from raw materials can result in the generation of hazardous waste due to (1) the formation of by-products, (2) the use of toxic catalysts, or (3) the use of toxic raw materials. Modification of the synthesis process can lead to substantial waste reduction. The following source reduction techniques were noted:

- Eliminate the use of toxic catalysts.
  Catalysts containing toxic metals are often used to manufacture dyes and pigments. Mercury catalyst used to produce anthraquinone dyes for the coloring of cottons was replaced with a less toxic substance (NJDEP 1985).

o Reduce the use of toxic raw materials.

Reduction of the toxicity of hazardous waste can be achieved through the elimination or reduction of the use of highly toxic reactants and intermediates. For example, since benzidine has been identified as carcinogenic, its use has been eliminated by most of the U.S. dye and pigment manufacturers (Radian 1977). In addition, some manufacturers who used to make intermediates for the production of anthraquinone dyes (which requires the use of toxic mercury catalysts) have stopped their production and import these intermediates instead (Catino and Ferris 1979, Bannister, Olin, and Stingle 1979, Fytelson 1982). While this measure will reduce the overall amount of hazardous waste generated in the U.S., it only shifts the problem to the foreign suppliers. In general, the use of less toxic substitutes should be explored most intensively in the area of auxiliary raw materials, i.e. those that do not undergo conversion to the final product. For example, the use of xylene as a solvent can be re-examined from the standpoint of substitution with less toxic solvent, e.g. acetone. Also, use of non-chromate treatment for cooling water will lower the toxicity of the blowdown sludge (which is not a part of "synthesis waste"--its inclusion is intended to illustrate the approach).

o Minimize byproduct formation.

Modifications of the synthesis process to increase yields and reduce by-product formation are extremely specific to the manufacturing of each different dye or pigment. Each process should be investigated separately to identify potential waste reduction techniques. To exemplify the approach, the following process modifications applicable to azo dyes were identified as candidates for future evaluation:

- Use an optimum pH range for a particular combination of diazo salt/coupling components. Since higher pH increases both the rate of the coupling reaction and the rate of formation of undesirable byproducts, it is likely that there is an optimum pH range which maximizes the yield of the desired product.

- Shorten the residence time before coupling to minimize the decomposition of diazonium salts. Since diazonium salts can readily

decompose in the coupling medium to produce phenolic compounds as byproducts, the time it takes to transfer these salts to the coupling reactor should be minimized. This can be accomplished by combining clarification operation with a fast transfer to the coupling reactor, e.g. by using a pump with the associated filter. The piping and filter casing can be emptied using pressurized nitrogen following the transfer. Pre-cooling of the coupling reactor would help to limit detrimental temperature rise.

In general, the avenues which may, upon exploration, lead to further increases in reaction yields and thusly to the decrease of byproduct waste generation include:

- search for more selective catalysts.
- modification of reaction temperature trajectory.
- modification of reaction addition strategy (rate of sequence).
- modifications to provide higher degree of mixing.

o Modification of filtration process.

By eliminating the need for filter aids, the amount of solid waste generated can be reduced. For cases in which a precoat-type pressure filter is being used for clarification, switching to a bag- or a leaf-type filter (LWVM 1985) would eliminate the need for filter aids, which does result in a reduction of the volume of discarded cake.

Generally, improvement in filtration efficiency will result in better product recovery and, subsequently, in less waste. Such improvement can be obtained through the use of multistage versus single stage filtration, the recycle of mother liquor during the initial cake-building period, the use of a cake-gasketed recessed plate instead of the conventional plate-and-frame (or the use of recessed plate filters to reduce leaking and wearing of the filter medium), or the use of low-temperature air to blow dry the filter cake to prevent the filter cloth's deterioration, which can result in leaking, and other techniques.

9.1.3 Product Finishing Wastes

Drying of dyes and pigments is done with rotary dryers, spray dryers, or drum dryers in hot air or in vacuum ovens. The following source control technique is proposed:

- Replace steam jets with vacuum pumps.
  In cases where steam jets are used to generate a vacuum, wastewater can be generated through contamination by process vapors or dusts of the cooling water used in the barometric condenser. This may represent a significant source of waste from the production of dyes which require extensive use of organic solvents (e.g. anthraquinone dyes). The wastewater generated can be avoided through the use of vacuum pumps with surface condensers. The use of a surface condenser will increase the potential recyclability of condensate.

Solid waste is generated from the collection of dust in baghouses during material handling, grinding, blending, and standardizing operations. The following source control techniques are noted:

- Use wet instead of dry grinding.
  Dye and pigment products can be ground wet using ball or sand mills and subsequently spray-dried. This operation will reduce the amount of dust emitted in comparison to the use of the conventional dry grinding step. This method is used only for water-insoluble dyes and pigments.

- Increase the use of dust suppression techniques.
  Dust emission can be suppressed through the use of atomized water sprays, enclosed weigh-transfer hoppers, or better care in manual material handling.

- Recycle baghouse fines.
  Baghouse hopper emptying should be scheduled for possible recycling of the dye or pigment fines. Baghouse hoppers should be cleaned before and after the manufacturing of a large quantity of a particular dye or pigment to recover these products. This practice is feasible only for plants producing a very limited number of dyes or pigments.

9.1.4 Equipment Cleaning Wastes

These constitute a significant fraction of the total waste generated during organic dye and pigment manufacture, which is typical for any batch process. The subject of how to minimize equipment cleaning waste is discussed in a separate study (#B22) found in this appendix, and is of universal importance to the entire chemical process industry. The reader is referred to that study for a general characterization of source control approaches.

Based on the information available, it appears that a two-step rinse with a maximum utilization of cleaning solution as a make-up in the next compatible batch is an approach utilized to a significant degree by the organic dye and pigment industry.

9.1.5 Spills and Off-Specification Product Waste

As previously mentioned, spills and off-specification products result from inadvertent operations usually attributable to human error. At times, such losses can also result from inadequate provisions for contingencies. For example, a diazotization reaction requires that solution is maintained at 32-40^{o}F, which necessitates the use of coolant maintained by a refrigeration system. If a refrigeration system malfunctions and coolant flow is stopped, the batch can be spoiled. Provision for an adequate surge capacity of chilled coolant may extend the time in which the refrigeration plant can be brought back on stream without spoiling the batch. In general, avoidance of spills and generation of off-spec products could be promoted by the following source control techniques:

- Increased use of automation.
  This includes automated batching systems, monitoring of the adequate number of process function, and automatic control of fail-safe and "fail-clean" shutdown features. Use of supervisory computer control is recommended for exploration.

- More intensive in-process quality control.

- More thorough cleaning of process equipment and piping.
  This measure would reduce contamination that may cause an off-spec batch.

- Better operating practice.
  This includes personnel training, better supervision, spill prevention programs, and other measures that fall under the category of procedural/institutional modifications. For a detailed discussion, the reader is referred to the separate study in this appendix.

9.2 Implementation Profile

Reduction of wastes from the manufacture of organic dyes and pigments can be achieved either through process modifications in the synthesis of the dye, or through improvements in operating practices in the area of product finishing, equipment cleaning and materials handling. A detailed characterization of optimal waste-reducing process modifications which lower the generation of synthesis waste is difficult to accomplish due to the large number of processes used to produce the wide variety of dyes and pigments currently on the market. Process modifications may require significant research and development expenditures and lengthy periods of time to become established. Given the shift from domestic production to imports, some companies may lack sufficient incentives to pursue additional development work.

Improvements in operating practices, on the other hand, are applicable to all processes. These are easily implemented as they typically require only minor changes in operational procedure or the addition of simple equipment or controls. However, they are not as effective as process modifications in reducing the generation of hazardous waste.

9.3 Summary

The sources of waste from the manufacture of organic dye and pigment and their respective source control techniques are summarized in Table 9-1. The ratings listed in the table are based on a scale of 0 to 4 and are used to evaluate each technique for

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE ORGANIC DYE / PIGMENT MANUFACTURING INDUSTRY

Waste Source	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Used Containers	1. Use liners and recyclable drums	1	1	3	3	2		2 3	0.4	0 4
	2. Maximize container size	1	1	2	3	1		1.5	0.1	
	3. Container segregation	1	1	3	3	1		2.3	0 2	
	Overall	1.00	1.00	2.67	3.00	1 33	0.02	2.3	0 2	0 4
Synthesis Waste (*)	1 Eliminate use of toxic catalyst	1	1	3	1	1		0 8	0 6	
	2. Eliminate use of toxic raw materials	1	1	3	1	2		0 8	1 1	1.1
	3. Minimize byproduct formation	1	1	3	3	3		2.3	0.6	
	4. Modify filtration process	0	0	1	3	2		0 8	0 1	
	Overall	0.75	0.75	2.50	2.00	2 00	0.60	2.3	0.6	1.1
Product Finishing Wastes	1. Replace steam jets with vacuum pumps	1	1	2	2	3		1.0	0.8	0 8
	2. Use wet grinding	0	0	3	3	1		2 3	0.2	
	3. Dust suppression	0	0	1	1	1		0 3	0 2	
	4. Recycle baghouse fines	0	0	2	0	1		0 0	0.5	
	Overall	0.25	0.25	2 00	1.50	1.50	0 05	2.3	0.4	0 8
Equipment Cleaning Wastes	1. See study on equipment cleaning (B22)	---	---	---	---	---		2 6	0 7	1.4
	Overall	---	---	---	---	---	0.32	2.6	0.7	1.4
Spills and Off-Specification Product Wastes	1. Increased automation	1	1	3	2	3		1 5	1 1	1 1
	2. Intensify quality control	1	1	2	3	2		1.5	0.3	
	3 Thorough equipment cleaning	1	1	2	3	2		1.5	0.3	
	4. Better operating practices	1	1	3	3	3		2.3	0.6	
	Overall	1.00	1 00	2.50	2.75	2 50	0.01	2.3	0.5	1 1
All Sources	All Methods						1.00	2.4	0.6	1.2

(*) These waste streams contain listed "F" and/or "K" RCRA wastes.

its waste reduction effectiveness, extent of current use and future application potential. The ratings were derived by project staff from the available information and from industry comments.

It appears that the current level of waste minimization in the manufacture of organic dyes and pigments is high. This is evidenced by the current reduction index (CRI) of 2.4 (60 percent) which measures the extent of reduction in the waste that otherwise would be generated if none of the listed methods were applied as they are currently.

The potential for future reductions appears modest, as evidenced by the future reduction index (FRI) of 0.6 to 1.2 (15 to 30 percent). The future reduction index is the measure of waste reduction achievable through implementation of the listed techniques to their rated extents. The greatest potential for future reductions appears to reside in eliminating the use of toxic raw materials and increasing the degree of automation within the production process.

10. PRODUCT SUBSTITUTION ALTERNATIVES

The production of organic dyes and pigments is inherently dynamic in nature since changes in the demands for these products are easily induced by several factors. Such factors include the possibility of creating new dyes with better qualities, the invention of new products that require completely different types of dyes for coloring purposes, or the improvement of existing dye technology which will affect the selection as well as the quantity of the dyes being used. For example, disperse dyes have attained wide usage due to the growth of synthetic fabrics. Furthermore, improvements in dyeing operations, such as increased use of automation, or the introduction of new dyeing techniques, such as low-liquor jet dyeing, will enhance the performance of one dye over another, and thus will make its selection more favorable. The growth of inactive dyes serves as a good example for this effect. Reactive dyes are used to color cellulose-based materials, and are preferred over other dyes due to their wide range of shades, excellent wet fastness, and simple application method. However, problems are encountered in the use of these dyes due to the low degree of exhaustion and fixation observed. This defect creates problems in the form of difficult pollution control and excessive energy usage which tend to discourage the use of these dyes. Research, however, is being done to counteract these problems through the use of fixation

accelerators or the development of short-liquor dyeing and low temperature dyeing techniques (Abeta, Yoshida, and Imada 1984). Once these barriers are overcome, the production of reactive dyes is expected to increase significantly.

In summary, changes in the dyeing industry, as well as increasing focus on the selection and manufacture of less toxic dyes and pigments, will significantly affect the future production of organic dyes and pigments.

11. CONCLUSIONS

Although significant waste reduction efforts have been made by the manufacturers of organic dyes and pigments, opportunities for potential future reduction remain numerous. Based on available information, an additional 15 to 30 percent of waste can probably be reduced if the proposed source reduction techniques are implemented. While source reduction measures associated with the dye synthesis stage of production are individually quite effective, implementation of these techniques can be difficult due to the diversity of the processes used to produce dyes and pigments in a single plant. Furthermore, the extent of waste reduction in one plant may differ greatly from another one. The most promising universal approach to waste reduction for synthesis stage, however, would be to eliminate the use of toxic raw materials, or to modify the existing process to achieve better product yield.

In addition to source reduction methods, changes in dyeing technology and/or the development of new materials by the textile industry can also significantly affect the production demand for organic dyes and pigments. This in turn can alter the waste load generated from the manufacturing process.

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13. INDUSTRY CONTACTS

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1. PROCESS: PAINT MANUFACTURE
2. SIC CODE: 2851
3. INDUSTRY DESCRIPTION

As defined by Standard Industrial Classification (SIC) 2851, the paints and allied products industry "comprises establishments primarily engaged in the manufacture of paints (in paste and ready mixed form), varnishes, lacquers, enamels and shellacs, putties, wood fillers and sealers, paint and varnish removers, paint brush cleaners, and allied paint products". Establishments engaged in the manufacture of pigments (organic or inorganic), resins, printing inks, adhesives and sealants, or artist materials are not included.

3.1 Company Size Distribution

Of the 1,441 paint manufacturing facilities located in the U.S. in 1982, more than 55 percent employed less than twenty people each. Overall, the Bureau of the Census (USDC 1985) estimated that 54,100 people were employed by the paint manufacturing industry. Table 3-1 lists company size distribution as a function of total number of employees at a given site.

Table 3-1 Company Size Distribution

	No. of Employees per Facility				
	Total	1-19	20-49	50-99	100+
No. of establishments	1,441	819	331	171	120
No. of employees	54,100	6,400	10,500	11,800	25,400

Source: 1982 Census of Manufacturers (USDC 1985).

3.2 Principal Producers

The paint manufacturing industry is composed of a small number of multi-plant, multi-product companies and a large number of single-plant companies. The eight major paint producing companies in the U.S. are listed below:

Sherwin-Williams	Clorox
PPG Industries	Valspar
SCM Corp (Glidden)	De Soto Paints
Inmont	Insilco Corp.

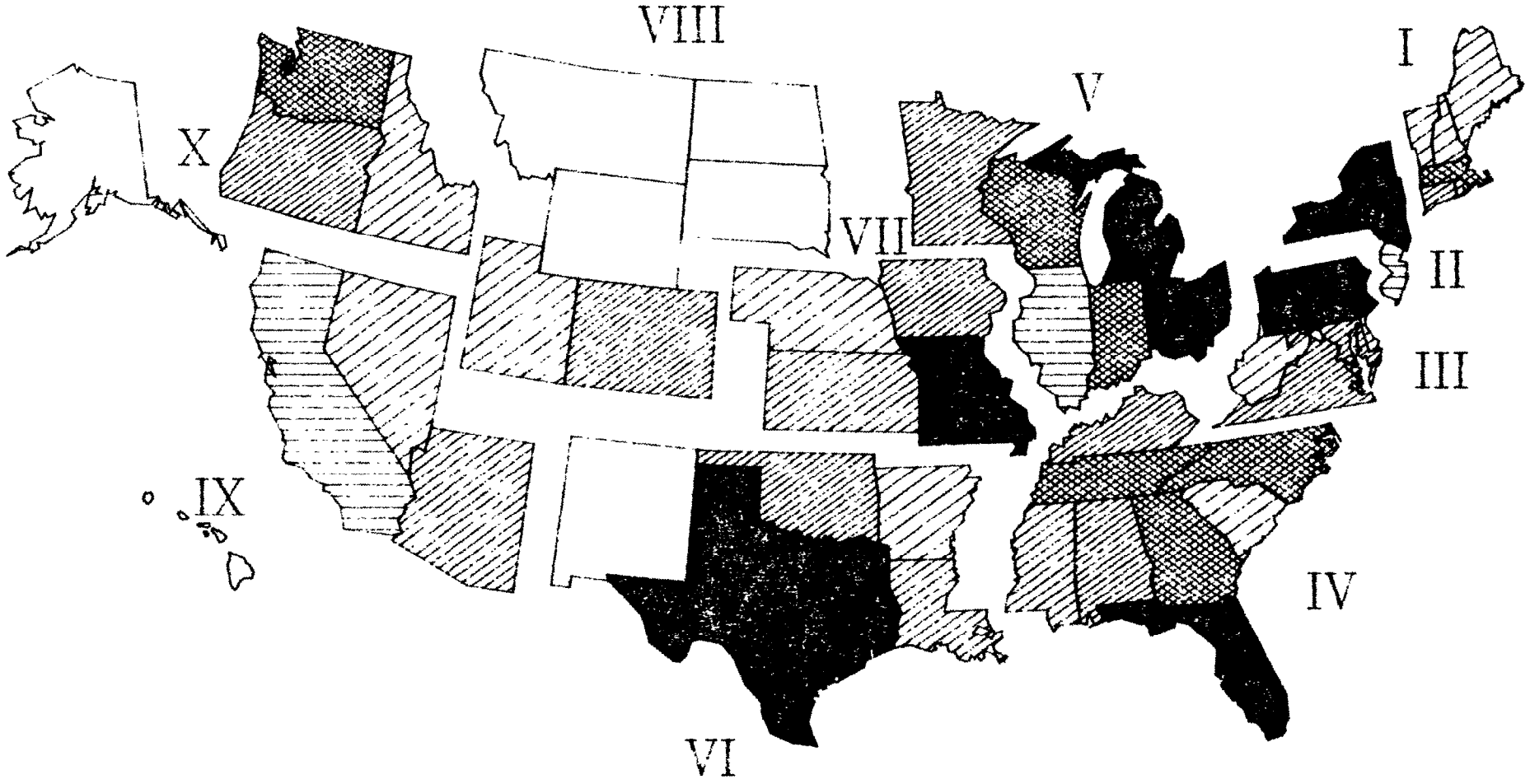
3.3 Geographical Distribution

Due to the expense of transporting products over long distances, paint plants tend to be clustered around population centers. Approximately 44 percent of all paint sites are located in five states (California, New Jersey, New York, Illinois, and Ohio), with 67 percent being located in ten states. Distribution by EPA regions are shown in Figure 3-1 and Table 3-2 below.

Table 3-2 Location of Facilities by EPA Region

EPA Region	No. of Employees per Facility		
	1-19	20+	Total
I	55	31	86
II	133	87	220
III	54	51	105
IV	110	99	209
V	191	168	359
VI	58	50	108
VII	46	31	77
VIII	12	5	17
IX	134	81	215
X	26	19	45
National	819	622	1441

Source: Assessment of Industrial Hazardous Waste Practices (WAPORA 1975) adjusted to reflect number of establishments listed in the 1982 Census of Manufacturers (USDC 1985).



Roman numerals show EPA regions

Figure 3-1 Paint Factories in the U.S.

4. PRODUCTS AND THEIR USE

Most small plants produce paint in 10 to 500 gallon batches. Plants with more than 20 employees tend to produce paint in 1,000 to 3,000 gallon batches*. Overall, the paint industry sold 8.6 billion dollars worth of product in 1983 ($3.9 billion for architectural coatings, $3.0 billion for product coatings, and $1.7 billion for special purpose coatings) (Webber 1984). The amounts and distribution of products manufactured by the paint industry in 1983 are shown below.

Table 4-1 1983 Paint Products and Use Distribution

Architectural Coatings	463 million gallons
Product Coatings	331 million gallons
Metal containers	19%
Automotive	16%
Machinery	6%
Sheet, strip and coil	6%
Metal furniture	5%
Other	48%
Special Purpose Coatings	130 million gallons
High performance maintenance	31%
Automotive and machinery refinishing	29%
Traffic paint	14%
Other	26%

Source: Chemical and Engineering News (Webber 1984).

For an average paint plant located in the U.S., 60 percent of its total annual production would be solvent-based paint, 35 percent would be water-based paint, and 5 percent would be allied products. While a large percentage of paint used for architectural coating is water-based (more than 70 percent), solvent-based paint is still predominately used for product and special purpose coatings.

5. RAW MATERIALS

Annual consumption rates of raw materials used by the paint manufacturing industry are shown in Table 5-1.

*Confidential source 1985: Personal communication.

Table 5-1 Raw Materials Used by the Paint Manufacturing Industry in 1982

Materials		Usage
Resins		1844 million lbs/yr.
	Alkyd	33%
	Acrylic	19%
	Vinyl	19%
	Other	29%
Solvents		3774 million lbs/yr.
	Aromatic	30%
	Aliphatic	27%
	Ketones	17%
	Alcohols	12%
	Other	14%
Pigments		1062 million lbs/yr.
	Titanium dioxide	65%
	Inorganic[a]	33%
	Organic	2%
Extenders		1162 million lbs/yr.
	Calcium carbonate	31%
	Talc	25%
	Clay	23%
	Other	21%
Miscellaneous		220 million lbs/yr.
	Drying Oils	41%
	Plasticizers	18%
	Other	41%

Source: Chemical Economics Handbook (SRI 1981) data for 1977 adjusted for 1982 production rates.

(a) Approximately 60 percent of the inorganic pigments used consisted of iron oxide, zinc oxide, zinc dust, and aluminum paste; 27 percent consisted of lead and chrome compounds; and 13 percent consisted of other.

The major raw materials used to manufacture paint are resins, solvents, drying oils, pigments, and extenders. Based on the wide variety of paints produced, no one type of material dominates the market.

6. PROCESS DESCRIPTION

Detailed process flow diagrams of paint manufacturing have been presented in the open literature (Haines 1954, Payne 1961). The following description briefly highlights the production of the industry's two main products: solvent-based paint and water-based paint. At a typical plant, both types of paint are produced. A block flow diagram of the steps involved in manufacturing paint is presented in Figure 6-1.

The production of solvent-based paint begins by mixing resins, ground pigment, and pigment extenders together in a high speed mixer. During this operation, solvents and plasticizers are also added. Following the mixing operation, the batch is transferred to a mill for additional grinding and mixing. The type of mill is dependent on the types of pigments being handled, so that no one style is universal. Next, the paint is transferred to an agitated tank where tints and thinner (usually a volatile naphtha or blend of solvents) are added. Upon reaching the proper consistency, the paint is filtered to remove any non-dispersed pigment and transferred to a loading hopper. From the hopper, the paint is poured into cans, labeled, packed, and moved to storage. The typical batch size for a small plant will range from 10 to 500 gallons while the average batch size for a large plant will be 1,000 to 3,000 gallons.

The typical paint plant produces about 60 percent solvent-based paint, 35 percent water-based paint, and 5 percent allied product. The water-based paint process is very similar to the solvent-based process. The major difference is the substitution of water for solvent and the sequencing of material additions. Preparation of water-based paint begins by mixing together water, ammonia, and a dispersant in a mixer. To this mixture, ground pigment and pigment extenders are added. After mixing, the material is ground in a mill and then transferred to an agitated mix tank. Four additions of materials occur in this tank. First, resin and plasticizers are added to the mixture; second, a preservative and an antifoaming agent are added; third, a polyvinyl acetate emulsion is added; and fourth, water is added as a thinner. Following this mixing operation, the handling of the paint is similar to that for solvent-based paints. At

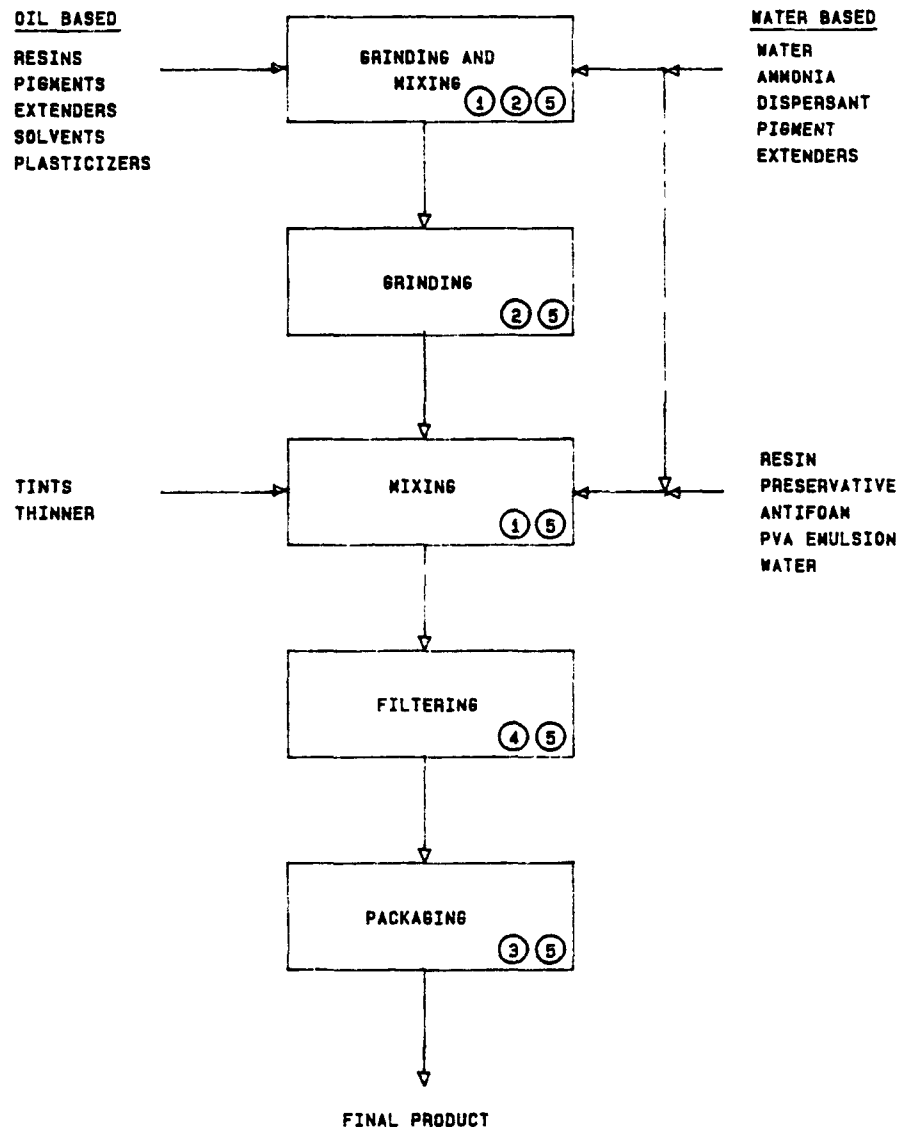


Figure 6-1 Block Flow Diagram for Paint Manufacture

many facilities the grinding and the mixing and grinding operation may be bypassed with all the dispersion operations occurring in a single high-speed mixer.

7. WASTE DESCRIPTION

Typically, paint facilities segregate and store waste only to the degree required by the waste disposal contractor. Since the degree of segregation can affect the amount of material having to be classified as hazardous, and the cost of disposing of hazardous material is increasing, paint facilities are taking a more active role in waste management. The major wastes that the paint industry must manage are empty raw material packages, dust from air pollution control equipment, off-specification paint, spills, and equipment cleaning wastes. Equipment cleaning wastes are a dominant waste stream.

The primary specific wastes associated with paint manufacturing are listed in Table 7-1. Waste generated by the industry is usually managed in one of four ways: on-site reuse, on-site recycling, off-site recycling, and off-site treatment/disposal (Ryan 1984). On-site reuse involves the reuse of waste (without treatment) as a feed or wash material for producing other batches of paint. Also included is the sale or in-house use of off-specification paint as utility paint. On-site recycling involves the reclaiming of solvent by distillation or recovery of heating values by incineration. Usually, on-site recycling is performed by large companies (those that produce more than 35,000 gallons of solvent waste each year) while small companies (those that produce 20,000 gallons or less per year) send the waste to an off-site recycler. The fourth option, off-site treatment/disposal involves incineration or land disposal. The extent of waste currently being land disposed is unknown.

8. WASTE GENERATION RATES

The most recent published estimates of the nationwide waste generation rates by paint industry date back to 1974 and are presented in Table 8-1 below. While the total amount of waste due to bags and packages was reported to be 302,000 metric tons per year (WAPORA 1975), the actual amount of hazardous waste (bags containing hazardous pigments) was only 2000 TPY. Since the estimate of 302,000 TPY included recycled drums and pallets, and because the current industry practice is to segregate hazardous from non-hazardous waste, only the hazardous amount is presented so as not

Table 7-1 Paint Manufacturing Process Wastes

No.	Waste Description	Process Origin	Composition	RCRA Codes
1.	Leftover raw materials in original containers	Unloading of materials into mixing tanks	Paper bags with a few ounces of left-over pigments	--
2.	Pigment dusts from air pollution equipment	Unloading of pigment into mixing tanks	Pigments	--
3.	Off-specification paint	Color matching (small scale) production	Paint	--
4.	Spills	Accidental discharge	Paint	--
5.	Waste rinsewater	Equipment cleaning using water and/or caustic solutions	Paint, water, caustic	--
6.	Waste solvent	Equipment cleaning using solvent	Paint, solvent	F002 F003 F005
7.	Paint sludge	Equipment cleaning sludges removed from cleaning solution	Paint, water, caustic, solvent	--
8.	Filter cartridges	Undispersed pigment	Paint	--

to distort the hazardous waste generation picture. In addition, the amount of solvent discarded only represents the amount of solvent considered by WAPORA to be toxic.

Current waste generation rates were not in evidence at the time of final document preparation. According to one source, these rates have changed dramatically in the last six years due to RCRA*.

Table 8-1 1974 Nationwide Generation Rates of Specific Wastes from the Paint Manufacturing Industry in metric tons per year

Wastestream	Total TPY	Toxic Solvents TPY	Toxic Metals TPY
Empty bags and packages	2,000	--	128
Dust from air pollution equipment	1,600	--	80
Off-specification product	4,900	580	41
Spills	5,400	85	5
Cleaning of Equipment	82,000	13,600	590
Total	95,900	14,265	844

Source: Assessment of Industrial Hazardous Waste Practices (WAPORA 1975).

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

The list of individual primary waste streams and their sources along with a list of source reduction methods is presented in Table 9-1. The following sections discuss recommended waste reduction methods and identified procedures. The basis for identification came from published accounts in the open literature and through industry contacts. It should be noted that not many published accounts were available. The reason for the lack of published data is probably that many of the methods used by the paint industry are common sense measures (i.e. good housekeeping) and are not viewed as being special waste reduction techniques worth extensive documentation, analysis, or presentation.

* National Paints and Coatings Association 1986: Personal Communication.

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" has also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel practices
  - Management initiatives
  - Employee training
- o Procedural measures
  - Documentation
  - Material handling and storage
  - Material tracking and inventory control
  - Scheduling
- o Loss prevention practices
  - Spill prevention
  - Preventive maintenance
  - Emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Bags and Packages

Inorganic pigments, which contain heavy metals and may therefore be classified as hazardous are usually shipped in 50 pound bags. After emptying the bag, an ounce or two of pigment usually remains inside. Empty containers of liquid raw materials that constitute hazardous waste (e.g. solvents and resins) are typically cleaned or recycled to the original raw material manufacturer or to a local drum recycler. Empty liquid containers are excluded from the following discussion. The following waste reduction techniques for bags and packages were noted:

- o Use of water soluble bags for toxic pigments and compounds used in water-based paints.

  When empty, the bags could be dissolved or mixed in with the paint. Such a method is commonly used for handling mercury compounds and other paint

fungicides*. This method could not be used, however, when producing high quality, smooth finish paint since the presence of this material could affect the paint's film forming property**.

- o Use of rinseable/recyclable drums with plastic liners instead of paper bags.

- o Better operating practices (Identified).
  Through industry contacts, it was established that the most effective way of reducing hazardous waste associated with bags and packages (or any other waste stream) was to segregate the hazardous materials from the non-hazardous materials As an example, empty packages that contained hazardous materials should be placed into plastic bags (so as to reduce or eliminate dusting which can lead to contamination of non-hazardous material and should be stored in a special container to await collection.

9.1.2 Pigment Dust from Air Pollution Equipment

Some of the dusts generated during the handling, grinding, and mixing of pigments can be hazardous. Therefore, dust collection equipment (hoods, exhaust fans, and baghouses) are provided to minimize a worker's exposure to localized dusting and to filter ventilation air exhaust. As of 1974, 15 percent of the pigment dust collected in baghouses was reused to make low-grade paint with the remaining 85 percent drummed for disposal (WAPORA 1975). The waste reduction methods considered consist of:

- o Dedicated baghouse system for pigment loading area (Suggested).
  At Daly-Herring Co., in Kinston, N.C., (while Daly-Herring is engaged in formulation of pesticides and not paints, there are many material handling problems common to both industries) dust streams from several different production areas were handled by a single baghouse. Since all of the streams were mixed, none of the waste could be recycled to the process that generated them. By installing separate dedicated baghouses for each production line, all of the collected pesticide dust recycled (Huisigh et al.

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* Confidental source 1985: Personal communication.
** E.I. Du Pont de Nemours & Co. 1985: Personal communication.

1985). While this example is not intended to imply that most of the dust generated by the paint industry could be recycled, it does show the overall importance of keeping waste streams segregated.

- Use of pigments in paste form instead of dry powders.
  Pigments in paste form are dry pigments that have been wetted or mixed with resins. Since these pigments are wet, less or no dust is generated when the package is opened. In addition, most pigments in paste form are supplied in drums (which can be recycled) and therefore would eliminate the waste due to empty bags. While this method would increase the amount of pigment handling occurring at the supplier's facility, it can be argued that the overall number of handling/transfer points for dry powder would be greatly reduced along with the probability of spills and dust generation.

- Better operating practices.
  Scheduled baghouse hopper emptying could be done to reduce the amount of hazardous waste generated. The major portion of solid waste collected by the air pollution equipment is titanium dioxide and extenders. Hazardous pigments make up only a small fraction of the waste and would only be present during colored paint production. Since many facilities produce colored paints on a non-continuous basis (i.e., once a week or once a month), scheduled cleaning of the equipment to coincide with colored paint production would allow for segregating the waste that contained hazardous pigments from that which did not.

9.1.3 Off-Specification Paint

Most off-specification paint is produced by small shops that deal in specialty paints. Since these paints cost more to produce, and therefore sell at a premium price, most off-spec paint is reworked into a salable product. Since elimination of off-spec paint production has built-in economic incentives, the following techniques are widely used:

- Increased automation.

- Better operating practices.

  Industry contacts indicated that better operating practices (better operator training, closer supervision, and tighter equipment inspection and maintenance), and increased use of automation were extremely effective at reducing the amount of waste generated. Overall, better operating practices are widely used by the paint industry while increased automation is just starting to be implemented. As the cost of digital electronic controls further declines, more of the paint industry is expected to take advantage of automation.

9.1.4 Spills

Spills are due to accidental or inadvertent discharges usually occuring during transfer operations or equipment failures (leaks). Spilled paint and the resulting clean up wastes are usually discharged to the wastewater treatment system or directly drummed for disposal. If the plant has floor drains, large quantities of water are used to clean up water-based paint spills. Dry cleaning methods (using sawdust) are employed for cleaning of solvent-containing spills or for water-based spills where floor drains are not available. The average amount of paint spilled at each facility is approximately 5 gallons per year, however, a few large spills can move it to 100 gallons per year (WAPORA 1975). Similar to the case of off-spec paint, waste reduction methods include:

- Increased automation.

- Better operating practices.

  The use of dry cleanup methods (sawdust, mopping) should be maximized wherever possible. By closing floor drains, employees are discouraged from grabbing a hose and washing down the area (WAPORA 1975, USEPA 1979). In addition, a large decrease in wastewater is achieved since the floors cannot be routinely washed.

9.1.5 Equipment Cleaning Wastes

For a general discussion of equipment cleaning in the process industries, the reader is referred to a separate study (#B22) included in this appendix. The text below discusses issues specific to the paint manufacturing process. Equipment cleaning is responsible for most of the waste generated during the paint manufacturing process. Following the production of either solvent or water-based paints, considerable waste or "clingage" remains affixed to the sides of the preparation tanks. The three specific methods of tank cleaning used in the paint industry are solvent washing for solvent-based paint, caustic washing for either solvent or water-based paint, and water washing for water-based paint.

Equipment used for preparation of solvent-based paint is rinsed with solvent, which is then generally reused in the following ways:

- Collected and used in the next compatible batch of paint as part of the formulation.
- Collected and re-distilled either on or off-site.
- Collected and used with or without settling for equipment cleaning until spent. When the solvent is finally spent, it is then drummed for disposal.

As of 1974, thirty-five percent of the solvent waste produced was recycled off-site and eight percent was recycled on-site (WAPORA 1975). Recycling of spent solvent is usually not practical whenever the solids concentration exceeds ten percent or the level of inhibitors and stabilizers in the recycled solvent is low. Of all the solvent that is recycled, seventy-five percent is recovered with the remaining portion disposed of as sludge.

Caustic rinse is used for equipment cleaning of both solvent and water-based paints. It is used more often with water-based paints, since water rinsing is usually insufficient in removing paint that has dried in the mix tanks. Solvent rinsing can usually remove solvent-based paint that has dried and therefore the need for caustic is reduced.

There are two major types of caustic systems commonly used by the paint industry. In one type of system, caustic is maintained in a holding tank (usually heated) and is

pumped into the tank to be cleaned. The caustic drains to a floor drain or sump from where it is returned to the holding tank. In the second type of system, a caustic solution is prepared in the tank to be cleaned, and the tank is soaked until clean. Most plants reuse the caustic solution until it loses most of its cleaning ability. At that time, the caustic is disposed of either as a solid waste or wastewater with or without neutralization.

Water wash of equipment used in the production of water-based paint is the source of considerable wastewater volume. Wastewater resulting from rinsing is usually handled as follows:

- Collected and used in the next compatible batch of paint as part of the formulation.
- Collected and used with or without treatment for cleaning until spent.
- Disposed with or without treatment as wastewater or as a solid waste in drums.

Sludges from settling tanks are drummed and disposed of as solid waste. Spent recycle rinsewater is drummed and disposed of as solid waste after the solubles content prohibits further use.

The percentage of solvent-base and water-base paints produced is the most important factor that affects the volume of process wastewater generated and discharged at paint plants. Due to their greater use of water-wash, plants producing 90 percent or more water-base paint discharge more wastewater than plants producing 90 percent or more solvent-base paint. Additional factors influencing the amount of wastewater produced include the pressure of the rinse water, spray head design, and the existence or absence of floor drains. Where no troughs or floor drains exist, equipment is often cleaned externally by hand with rags; when wastewater drains are present, there is a greater tendency to use hoses. Several plants have closed floor drains to force use of dry clean-up methods and discourage excessive water use.

Waste associated with equipment cleaning represents the largest source of waste in a paint facility. Methods that reduce the need or frequency of tank cleaning or allow

for reuse of the cleaning solutions are the most effective. Waste reduction methods considered include:

- Use of mechanical devices such as rubber wipers.
  In order to reduce the amount of paint left clinging to the walls of a mix tank, rubber wipers are used to scrape the sides of the tank. This operation requires manual labor and hence the percentage of waste reduction is a function of the operator*. Since the benefits will be offset by increased labor, mechanization/automation should be considered. Many new mixers are available that are designed with automatic wall scrapers (Weismantel and Guggilam 1985). These mixers can be used with any cylindrical mix tank (flat or conical bottom).

- Use of high pressure spray heads and limiting wash/rinse time.
  After scraping the tank walls, high pressure spray hoses can be used in place of regular hoses to clean water-based paint tanks. Based on studies (USEPA 1979), high pressure wash systems can reduce water use by 80 to 90 percent. In addition, high pressure sprays can remove partially dried-on paint so that the need for caustic is reduced. Tanks used for making solvent-based paints normally employ a built-in high pressure cleaning system. At Lilly, in High Point, N.C., a high pressure cleaning system was installed in several mix tanks. By continuously pumping a fixed amount of solvent into a tank until it was clean, the overall volume of solvent required for cleaning was reduced (Kohl, Moses, and Triplett 1984).

- Use Teflon** lined tanks to reduce adhesion and improve drainage.
  The reduced amount of "clingage" will make dry cleaning more attractive. This method is probably applicable only to small batch tanks amenable to manual cleaning.

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* Confidential source 1985: Personal communication.
** Registered trademark of E.I. Du Pont de Nemours & Co.

- Use a plastic or foam "pig" to clean pipes.

  It was reported that much of the industry is currently using plastic or foam "pigs" (slugs) to clean paint from pipes*. The "pig" is forced through the pipe from the mixing tank to the filling machine hopper. The "pig" pushes ahead paint left clinging to the walls of the pipe. This, in turn, increases yield and reduces the subsequent degree of pipe cleaning required. Inert gas is used to propel the "pig" so as to minimize drying of paint inside the pipe. Piping runs and the equipment (launcher and catcher) must be carefully designed so as to prevent plugging, spills, sprays, and potential injuries.

- Better operating practices.

  At Desoto, in Greensboro, N.C., wash solvent from each solvent-based paint batch is separately collected and stored. When the same type of paint is going to be produced, waste solvent from the previous batch is used in place of virgin solvent. In 1981, Desoto produced 25,000 gallons of waste mineral spirits. In 1982, when the system was implemented, waste solvent production amounted to 400 gallons. This same technique is currently being applied to their latex paint production operation (Kohl, Moses and Triplett 1984).

  At Thiele-Engdahl, in Winston-Salem, N.C., a similar procedure of solvent segregation and reuse was attempted. However, due to the large variety of products made, segregation proved to be too complicated. In addition, the high cost of raw materials (Thiele-Engdahl produces specialty inks for rotogravure printing) and the risk of contaminating the entire batch far outweighed the savings in virgin solvent cost (Kohl, Moses and Triplett 1984).

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* E.I. Du Pont de Nemours & Co. 1986: Personal communication.
National Paint and Coating Association 1986: Personal communication.

Other waste reduction measures based on good operating practices would be to schedule paint production for long runs or to cycle from light to dark colors so that the need for equipment cleaning would be reduced. For facilities using small portable mix tanks for water-based paints, immediate cleaning after use would reduce the amount of paint drying in the tank and hence reduce the need for caustic. Many times, dirty equipment is sent to a central cleaning operation where it waits until a given shift (usually night) to be cleaned*. While tanks wait to be cleaned, the residual paint dries up often necessitating the use of caustic solution for cleaning. Avoidance of accumulation of dirty tanks can be achieved by designing and performing the cleaning operation to handle any peak load continuously. This would reduce the need for caustic cleaning and promote water cleaning instead.

For plants employing CIP (clean-in-place) recycle systems for wash/rinse operations, the inventory replacement frequency (and therefore waste volume) can be minimized by using these waste reduction methods:

- Use of a countercurrent rinsing sequence.
  For facilities that have additional storage space available, countercurrent rinsing can be employed. This technique uses recycled "dirty" solution to initially clean the tank. Following this step, recycled "clean" solution is used to rinse the "dirty" solution from the tank. Since the level of contamination builds up more slowly in the recycled "clean" solution than with a simple reuse system, solution life is greatly increased. Countercurrent rinsing is more common with CIP systems, but can be used with all systems.

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*Confidential source 1985: Personal communication.

- Sludge dewatering by filtration or centrifugation.
  Sludge removed from spent rinse water can be dewatered so as to minimize total waste volume. Several paint plants have installed belt filters and are assessing their effectiveness*. At some facilities, dewatered sludge (which still contains solvents and resins) is mixed with paint sludge from solvent recovery and incinerated. For facilities not producing solvent-based paint, incineration would not be an attractive option since the heating value of the sludge would be low. In addition, the capital cost and regulatory requirements for building an incinerator could be prohibitive to all but the largest producers.

- Provision for adequate solid settling time in spent rinse solution.

- Use de-emulsifiers in rinse water to promote emulsion breakdown and organic phase separation.

Another item included under the heading of cleaning wastes are the used filter cartridges produced during the paint loading operation. These cartridges are designed to remove undispersed pigment from the paint during loading and will be saturated with paint when removed. Hence, waste minimization and economy both call for as small a cartridge as possible so as to reduce the amount of paint lost and the capital spent for the filters. If frequent filter plugging is a problem, then it should be first addressed from the standpoint of improving pigment dispersion, and not from the standpoint of increasing filter area.

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*Confidential source 1985: Personal communication.

9.2 Implementation Profile

The main source reduction methods discussed for use by the paint industry include segregation of solid waste by prior content, reduction or elimination of hazardous pigments (hazardous pigments that could not be eliminated should be used in paste form), use of wipers on mix tanks, high pressure spray systems, use of countercurrent rinse sequence on tanks, and sludge dewatering before sending it to a landfill. Reuse of cleaning solutions as part of paint formulation is promoted by good operating practices which include segregation. Incineration of sludges (especially from solvent-based operations) destroys the organics present, but still may produce toxic inorganic residuals requiring dispoal. Since incinerators are difficult and expensive units to build, operate, and maintain, their use is only practical at large paint facilities.

While segregating solid waste by prior content and reducing the use of hazardous pigments would not be difficult to implement, fitting all tanks with wipers would be difficult. Square tanks would require custom modification and installation, since the wiper could not be installed on the mixer (the normal method of installation). Retrofitting existing mixers with wipers is impossible since most mixers used by the paint industry are single-shaft and a mixer/wiper unit requires a dual shaft. Therefore, mixer/wiper units would only be considered for new installations or as replacements. Since much of the hardware in the paint industry is over 20 years old, detailed return on investment analysis could be performed to determine if a unit should be repaired or replaced. Because the cost of repairing a unit can range from 2,500 to 10,000 dollars, replacement could be an attractive alternative (Weismantel and Guggilam 1985).

Installation of a high pressure spray system would require the installation of a pump and some piping at each cleaning station. While the space requirements for a pump are small, the layout of the additional piping would have to be given special attention so as not to impede operations in the area. The economics of a high pressure spray system has been worked out in detail (USEPA 1979), with the average cost running about 20,000 dollars per system. Using a countercurrent rinse sequence and dewatering sludges would require installation of at least two cleaning solution storage tanks and a belt filter or similar unit. Besides the added space requirements for these units and the significant capital cost, operators would need to be fully versed in the

theory and method of their operation. The economics of installing a filter unit and/or sludge incinerator has been addressed in detail elsewhere (WAPORA 1975, USEPA 1979). For all but the largest of producers, the cost of installing, operating, and maintaining the units was prohibitive.

When viewed in light of increasing hazardous waste disposal costs, many of the waste reduction measures identified appear economically practicable. By segregating wastes, savings in disposal costs could be achieved at little cost to the facility. No special equipment would be required and the additional labor would be minor. While reducing or eliminating the use of hazardous pigments would also be easily implementable, the economic costs would be much greater: either higher costs for using less hazardous pigments would have to be incurred or the company would have to forego competing in a given market, e.g. red lead primer.

9.3 Summary

Table 9-1 presents summary data on paint industry waste sources and control methods. The ratings shown in the table for each of the noted methods were based on review of the available literature and consultations with industry personnel. Based on the measures already undertaken by the paint manufacturing industry, the waste appears to have been minimized significantly to a level characterized by a current reduction index of 2.2 (55 percent). The index is a measure of reduction relative to the waste that would have been produced if none of the measures listed were applied at their current level. By implementing additional waste reduction measures or increasing the use of existing measures, the amount of waste currently being generated can be reduced to a level characterized by a future reduction index of 0.7 to 1.7 (18 to 43 percent) which is indicative of a moderate to significant potential for reduction.

Based on the extent of waste generated due to equipment cleaning, it appears that installation of a high pressure wash system and further implementation of better operating practices are the two most effective measures that can be taken. Of the remaining control methodologies, use of "pigs" to clean lines, dewatering of spent rinse sludge, and increased use of automation also show high promise, as evidenced by their high individual future reduction indexes.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE PAINT MANUFACTURING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Leftover Inorganic Pigments in Bags and Packages	1. Use water soluble bags and liners	1	0	3	1	0		0.8	0.0	
	2 Use recyclable/lined containers	1	0	2	1	1		0.5	0.4	
	3. Implement better operating practices	1	0	3	2	2		1.5	0.8	0.8
	Overall	1.00	0.00	2 67	1 33	1 00	0.02	1.5	0.4	0 8
Pigment Dust from Baghouses	1. Install dedicated baghouse systems	1	1	2	1	1		0.5	0.4	
	3. Use pigments in paste form	1	1	3	1	3		0.8	1.7	1.7
	3. Implement better operating practices	1	1	2	1	1		0.5	0.4	
	Overall	1.00	1 00	2.33	1 00	1.67	0.02	0.8	0 8	1.7
Off-Specification Paint	1. Increased use of automation	3	1	4	1	2		1.0	1.5	1.5
	2. Implement better operating practices	3	2	4	3	2		3.0	0.5	
	Overall	3.00	1.50	4.00	2.00	2 00	0.05	3.0	1.0	1 5
Spills	1. Increased use of automation	3	1	4	1	2		1 0	1.5	
	2. Maximize use of dry clean-up methods	3	1	3	1	3		0.8	1.7	1 7
	3. Implement better operating practices	3	2	4	3	2		3 0	0.5	
	Overall	3 00	1.33	3 67	1.67	2.33	0.06	3.0	1.2	1 7
Equipment Cleaning Wastes (*)	1 Use mechanical wipers on mix tanks	3	1	2	1	1		0.5	0.4	
	2. Install high pressure wash system	3	2	3	1	3		0 8	1.7	1.7
	3. Install Teflon liners on mix tanks	0	0	1	0	1		0.0	0.3	
	4. Use foam/plastic "pig" to clean lines	1	1	3	2	2		1.5	0.8	
	5. Implement better operating practices	3	2	4	2	2		2.0	1.0	
	6 Use a countercurrent rinse sequence	1	1	3	1	1		0.8	0.6	
	7 Dewater spent rinse sludge	3	2	3	2	2		1.5	0 8	
	8. Increase spent rinse settling time	0	0	1	0	1		0.0	0.3	
	9 Use de-emulsifiers on spent rinse	0	0	1	0	0		0.0	0.0	
	Overall	1.56	1.00	2 33	1 00	1 44	0 85	2 0	0.6	1 7
All Sources	All Methods						1 00	2.2	0.7	1.7

(*) These waste streams include listed "F" and/or "K" RCRA wastes

10. PRODUCT SUBSTITUTION ALTERNATIVES

By altering the composition of paint, the amount and toxicity of hazardous materials (and the overall toxicity of the paint itself) required to be landfilled can be reduced. Another way of reducing waste associated with paint production would be to reduce the demand and therefore the production of paint. By producing a paint with a longer life span or by utilizing building materials that do not require painting (e.g., precolored concrete, stucco, vinyl coated siding, brick), a reduction in the amount of architectural coatings produced could be achieved. Reductions in the demand for product coatings could occur by increasing the use of powder or plastic coatings. A complete environmental assessment of each alternative is required before its overall benefits and disadvantages can be determined. Such an assessment was not performed; therefore, no specific product substitutions can be recommended.

10.1 Pigment Substitution

Two cases of pigment substitution were identified. The first case concerned the use of lead pigment. While the paint industry has eliminated the use of lead to a large extent, a market still exists for red lead primers (red lead makes an excellent primer and few substitutes exist). Most plants produce a wide variety of paints, and typically, red lead primers represent a small percentage of a plants' total output. A commitment by management not to produce red lead primer would eliminate the need to manage lead pigments (the loss of this market would have to be weighed against handling and disposal costs for each facility). Because of the increasing regulations on the use of all lead pigments, some plants have ceased production of lead primer*.

The second case involves chrome yellow. Chrome yellow is used mainly in traffic paint and provides a very bright color. In order to avoid the use of chrome yellow in other products, some companies have switched to organic pigments (expensive) or to yellow iron oxide (dirty color). One such company is Environmental Inks and Coatings Corporation in Morganton, N.C. (Kohl, Moses, and Triplett 1984). Again a commitment by management is required in light of the added expense versus disposal cost savings. Customer's specifications stand in the way of total elimination of chrome yellow use, since it is required to be used in yellow traffic paint*.

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* Confidental source 1985: Personal communication.

In weighing the environmental pros and cons of toxic pigment substitution with less toxic alternatives, it must be noted that the use of heavy metal pigments in product coatings extends the durability of the product*. It is also important to note that substitution of pigments in existing formulations will alter both the color and performance of the coating; hence, it must be done with the approval of changed specifications by a customer.

10.2 Increased Quality of Home Market Paints

While most paint sold is of very high quality (commercial architectural coatings, product coatings, and special purpose coatings have very long lifetimes), paint sold to the home market can vary widely. This is due, in part, to market conditions that demand that a paint producer supply a low cost paint if he wishes to remain competitive. If the home consumer showed preference for a higher quality paint, then the production of lower quality paints would decrease. In addition, less paint would be produced overall each year since the need for repainting would be lessened. Related to this issue is the level of consumers' awareness as to the proper ways of selecting and applying paint. If the level of awareness is found to be low, then consumer education efforts could be conducted through various approaches, such as dissemination of information about paint application economics. Additionally, durability of coatings can be promoted by improvement of the general knowledge of proper application techniques, specifically, surface preparation. Even the highest quality paints will perform poorly if misapplied or if they are inappropriate for the job.

10.3 Architectural Coating Substitutes

Many substitutes exist for architectural coatings. For building exteriors, anodized metal, brick, marble, glass, colored concrete, and vinyl coated sidings have been used. For interiors, wood paneling, fabric coverings, and wallpaper are very popular. Since the use of these materials is mostly for aesthetic rather than functional purposes, each one's position in the market place will fluctuate based on demand.

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* National Paint and Coatings Association 1986: Personal communication.

10.4 Product Coating Substitutes

Unlike some architectural coatings, product coatings must provide functional protection as well as an aesthetic function. Recent substitutions that are finding a market place are powder and plastic coatings. Because powder coatings contain no solvent and most of the waste generated can be recycled, equipment manufacturers view powder coatings as a way of meeting EPA standards. Coupled with the savings in energy and labor, there is increased productivity. It is expected that the current share of the powder coating market (5 to 6 percent in 1983) will increase to 15 percent by 1993. While numbers were not reported for the U.S., some European finishers report that over 70 percent of all new production lines being installed are powder (Church 1984).

11. CONCLUSIONS

While the paint industry has done much to reduce the amount of waste it produces, it appears that further reductions are possible. Our estimates indicate that future waste reduction potential can be characterized as significant with reductions ranging from 18 to 43 percent. Several methods that appear to be quite effective and feasible for future implementation were identified and include high pressure spray systems for cleaning of water-based paint manufacturing equipment, further implementation of better operating practices, use of "pigs" for cleaning lines, dewatering of wastewater sludge, and increased use of automation. Reductions will occur as more and more facilities initiate and continue waste reduction programs and as older equipment wears out and is replaced.

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13. INDUSTRY CONTACTS

Confidential sources

Dr. G.J. Hollod, Senior Environmental Engineer, Petrochemical Dept., E.I. du Pont de Nemours & Co. Wilmington, DE.

R.J. Nelson, Associate Director, Environmental Affairs Technical Division, National Paint and Coatings Association, Washington, D.C.

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1. PROCESS: PETROLEUM REFINING
2. SIC CODE: 2911
3. INDUSTRY DESCRIPTION

The petroleum refining industry is comprised of establishments primarily engaged in the manufacture of gasoline, kerosene, distillate and residual fuel oils, lubricants and other products from crude petroleum and its fractionation products. Excluded from this industry are establishments engaged in producing natural gasoline from natural gas, the manufacture of lubricating oils and greases by blending purchased materials, and those re-refining used lubricating oils.

3.1 Company Size Distribution

Table 3-1 presents the number of establishments and number of employees for the petroleum industry in 1982. Output and employment in the industry is dominated by the larger establishments. The largest 65 of the 434 petroleum refining establishments accounted for more than 65 percent of the total industry employment and more than 63 percent of the total industry output in terms of value added by manufacture.

Table 3-1 1982 Company Size Distribution

	No. of employees per facility				
	1-99	100-499	500-999	1000+	Total
No. of establishments	241	128	41	24	434
No. of employees	6,600	31,300	27,700	43,200 (a)	108,800

Source: 1982 Census of Manufacturers (USDC 1985).

(a) Excludes totals for two establishments with more than 2500 employees to avoid disclosure of individual company data.

3.2 Principal Producers

In 1982, the following companies maintained the largest refining capacities in the United States:

Exxon	Gulf Oil
Standard Oil of California	Atlantic Richfield
Standard Oil of Indiana	Mobil
Shell (Royal Dutch) Oil	Phillips Petroleum
Texaco	Marathon Oil

3.3 Geographical Distribution

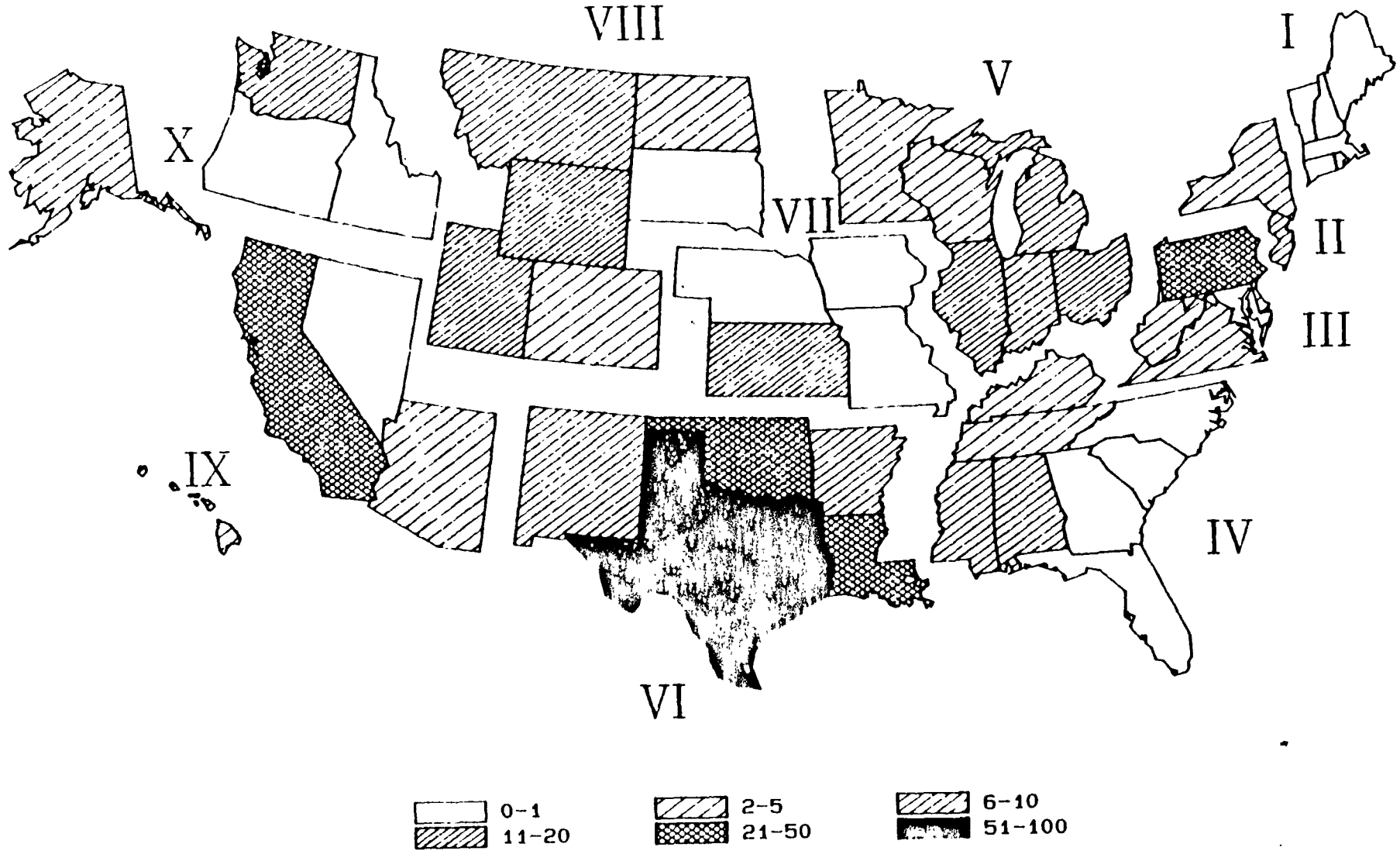
Table 3-2 and Figure 3-1 shows the number of petroleum refining establishments by EPA region. EPA Region VI contained 171 petroleum refineries in 1982, or approximately 40 percent of all establishments. Region IX, containing 54 refinery establishments, and Region V, containing 52 establishments, also contained large numbers of refineries. The four leading states in employment were Texas, California, Louisiana, and Pennsylvania, accounting for 64 percent of the industry's employment.

Table 3-2 Location of Facilities by EPA Region

EPA Region	Number of Establishments
I	--
II	14
III	34
IV	21
V	52
VI	171
VII	13
VIII	30
IX	54
X	11
National	400(a)

Source: 1982 Census of Manufacturers (USDC 1985).

(a) Establishments in states with less than 150 employees in the petroleum refining industry are not included.



Roman numerals show EPA regions

Figure 3-1 Petroleum Refineries in the U.S.

4. PRODUCTS AND THEIR USE

The types of products shipped and the dollar value of these shipments in 1982 are presented in Table 4-1. Gasoline, light fuel oils, jet fuel, and heavy fuel oil shipments accounted for over 80 percent of the total value of product shipments from the petroleum refining industry.

Table 4-1 1982 Product Shipments by the Petroleum Refining Industry

Product	Shipment Value (millions) $	Percentage of Total Shipment Value
Gasoline	95,115	49.7
Jet fuel	14,862	7.8
Kerosene	1,887	1.0
Light fuel oils	37,298	19.4
Heavy fuel oils	11,391	6.0
Lubricating oils and greases made in refineries	2,891	1.5
Unfinished oil and lubricating oil base stock	8,066	4.2
Asphalt	2,980	1.6
Liquified refinery gases	8,396	4.4
Aromatics	1,354	0.7
Other	7,130	3.7
Total	191,370	100.0

Source: 1982 Census of Manufacturers (USDC 1985).

5. RAW MATERIALS

The types of materials consumed as feedstock by the petroleum refining industry in 1982 are presented in Table 5-1. The delivered cost of each material type is also shown. Crude petroleum is the major raw material consumed by the petroleum

refining industry, representing over 80 percent of the total delivered cost of all materials consumed by the industry in 1982.

Table 5-1 Raw Materials Consumed by the Petroleum Refining Industry in 1982

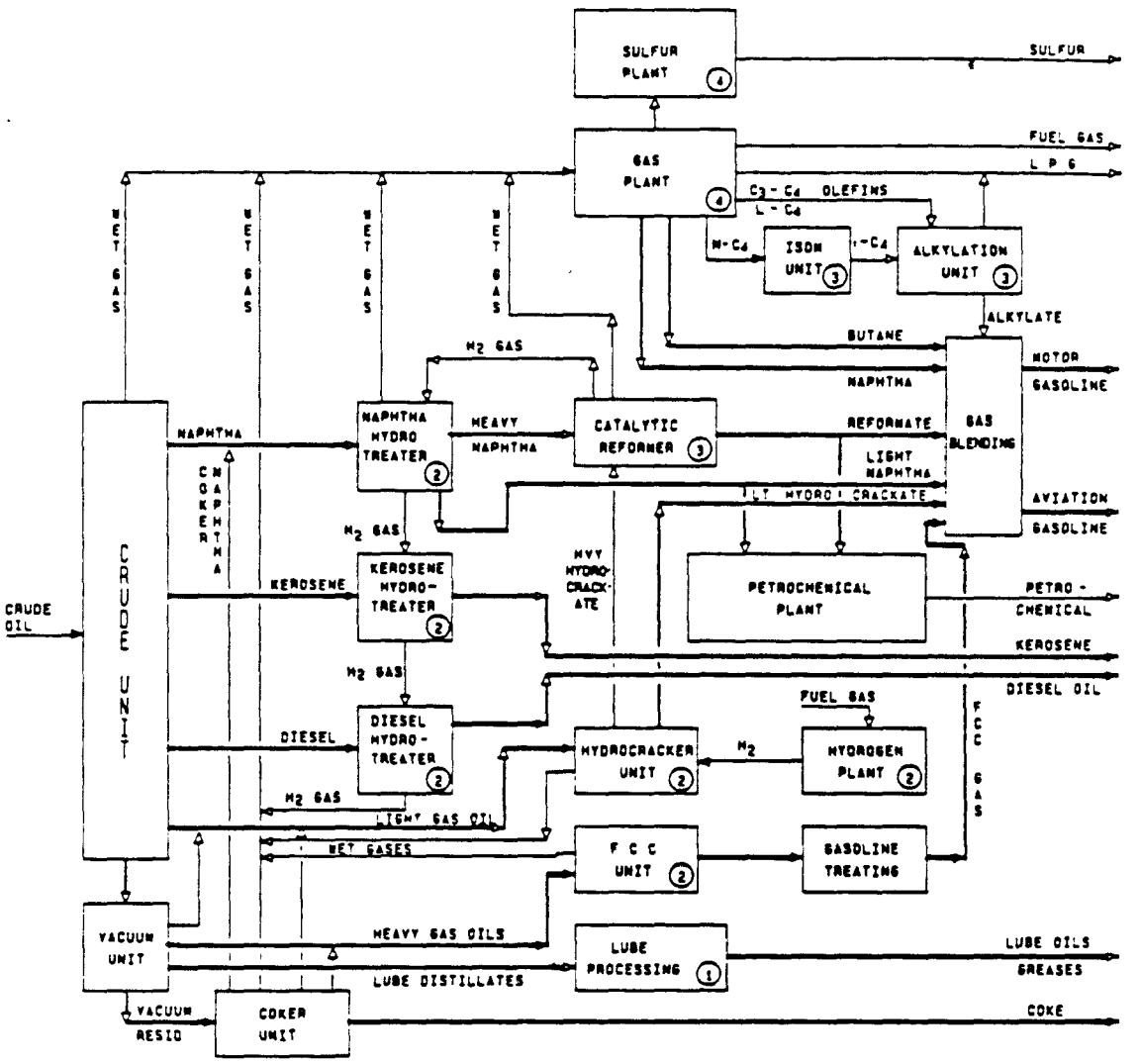
Material	Delivered Cost (millions) $	Percentage of Total Delivered Cost
Crude petroleum	137,870	82.7
Unfinished oils	558	0.3
Natural gas liquids	7,901	4.7
Benzol	74	--
Toluene and xylene	459	0.3
Additives	1,199	0.7
Chemical catalytic preparations	679	0.4
Caustic soda	80	0.1
Sulphuric acid	120	0.1
Containers	156	0.1
Other	17,742	10.6
Total	166,838	100.0

Source: 1982 Census of Manufacturers (USDC 1985).

6. PROCESS DESCRIPTION

Crude oil contains a wide variety of hydrocarbon compounds which range from light gases to residual fractions that cannot be separated by distillation. Crude oil is made up primarily of paraffin compounds, olefins, naphthenes, and aromatics in varying proportions. Apart from carbon and hydrogen, the elemental analysis shows sulfur, oxygen, nitrogen and heavy metals present in small quantities.

Most refinery processes fall into one of three classifications: separation, conversion, or upgrading. Detailed descriptions are available in the literature (Jahnig 1982, Shreve 1967). The following discussion highlights the main process activities. For convenience, an overall block flow diagram is presented in Figure 6-1.



PROCESS WASTE CATEGORIES

(1) SEPARATION PROCESS WASTES (FILTER CLAYS)

(2) CONVERSION PROCESS WASTES (CATALYST FINES/ SPENT CATALYST)

(3) UPGRADING PROCESS WASTES (SPENT CATALYST/ SLUDGE)

(4) AUXILIARY PROCESS WASTES (SPENT AMINE/ STRETFORD SOLUTION)

NOTE EQUIPMENT CLEANING WASTES WASTEWATER TREATMENT WASTES AND UTILITY PRODUCTION WASTES ARE NOT SHOWN

Figure 6-1 Process Block Flow Diagram for a Typical Refinery

6.1 Separation Processes

Separation processes are used to provide feedstocks of specified physical and chemical properties to other refining unit processes. Typical separation processes are desalting, primary distillation, deasphalting, solvent refining, and lube oil finishing. These operations are discussed individually below.

The first step in crude oil refining is the desalting operation. Crude oil typically contains salts, water, and suspended matter in the form of droplets or as a fine emulsion. These materials are present naturally in the oil and also may be introduced during shipping or storage. It is particularly important to remove these contaminants so as to avoid corrosion or plugging and buildup problems in the refinery equipment. The crude oil is pumped from storage into the heated desalter unit. Some of the larger droplets settle out during storage. The remaining droplets and emulsified materials are removed by the addition of water and flocculants. The oil/water emulsion is separated by electrostatic precipitation with 95 percent removal efficiency.

Distillation follows the desalting process. Typically, the crude oil is separated or "cut" into three categories of products, each cut differentiated by boiling range. These products are: naphtha, middle distillate, and a heavy bottoms residual. Also from this process, light fractions (C_1 to C_4 hydrocarbon) are recovered for further purification in the gas treating operation.

The naphtha cut is the primary precursor to motor gasolines. It is upgraded by hydrotreating (primarily to remove sulfur, oxygen, and metals) and then further improved by the process of reforming. The middle distillate cut includes jet fuel, diesel, and home heating oil. The end point of the middle distillate cut is about 300°C (Jahnig 1982). Fractions boiling above this temperature come out in the bottoms cut. The bottoms fraction provides feed-stock for the vacuum distillation process. The vacuum stills remove the remaining heavy gas oil not recoverable in the atmospheric stills, and provide asphalt and lube oil stocks and coker feed. The residue from the vacuum stills goes to the coker where the volatiles are removed, leaving coke as the final product.

Deasphalting removes asphalt or resins from the bottoms fractions, to produce stocks suitable for subsequent lube oil or catalytic cracking processes. The asphaltic

materials are extracted through the use of a solvent, such as propane. The process is carried out in an extraction tower, where pipe still bottoms or other heavy stock are mixed with propane. After the asphalt has been removed the propane is recovered.

Solvent refining includes a large number of alternative subprocesses designed to obtain high-grade lubricating oil stocks or aromatics from feedstocks containing naphthenic, acidic, organometallic, or other undesirable materials. Basically, it is a solvent extraction process dependent on the differential solubilities of the desirable and undesirable components of the feedstock. The principal steps are countercurrent solvent extraction, separation of solvent and product by heating and fractionation, removal of trace solvent from the product, and solvent recovery. Recent advances in solvent refining include a Residuum Oil Supercritical Extraction (ROSE) method developed by Kerr-McGee Refining Corporation (Anon. 1981).

Lube oil finishing is used to further refine solvent-refined or dewaxed lube oil stocks, and involves clay or acid treatment to remove color-forming and other undesirable materials. The two methods most widely used by industry are continuous contact filtration in which the oil-clay slurry is heated and the oil removed by vacuum filtration; and percolation filtration, in which the oil is filtered by percolation through clay beds. Percolation also involves naphtha washing and kiln burning of spent clay to remove carbon deposits and other impurities from the clay so it can subsequently be reused.

6.2 Conversion Processes

Many primary distillation products undergo some form of conversion operation. Conversion processes are used to purify or change the chemical and/or physical properties of the distillates, usually by breaking large molecules into smaller ones. Typical conversion processes are hydrotreating, catalytic and thermal cracking, hydrocracking, and coking.

In most refineries, usually only the naphtha and middle distillate cuts or low metals content residuum are hydrotreated. The hydrotreating process converts the heavier components of these cuts to lower boiling products by mild cracking and by adding hydrogen to the molecules using a fixed bed catalytic reactor. The reactor products are cooled, and the hydrogen with impurities and high grade product are separated.

Among the catalysts most commonly used in hydrotreating is cobalt molybdate with various promoters on silica-alumina supports.

Hydrotreating was first used primarily on the relatively clean lighter feedstocks, but with more operating experience and improved catalysts, hydrotreating has been applied to increasingly heavier fractions. The process improves the quality of the feed to subsequent operations by removing sulfur compounds, nitrogen, oxygen, and metals carried over from primary distillation. Hydrotreating of kerosene, jet, and diesel fuel components stabilizes and saturates the diolefins and other compounds which form gums and deposits. Fixed catalyst bed hydrotreating of atmospheric or vacuum still heavy oils has been limited to those feedstocks where the metals content is low. The metals quickly degrade the catalysts by buildup and subsequent pore blocking. In recent years, progress in applied catalysis has resulted in the development of longer-life hydrotreating catalysts. Along with hydrocracking, hydrotreating is one of the most rapidly growing refinery processes.

Cracking includes fluid catalytic cracking, thermal cracking, hydrocracking, visbreaking, and coking. The old process of thermal cracking, or now more generally applied, fluidized-bed catalytic cracking, are processes used on the heavy distillates from the vacuum still. In each of these operations, heavy oil fractions are broken down into lighter fractions such as gasoline, domestic heating oil, etc. At this time, about half of the gasoline sold in the United States is obtained from petroleum by fluidized bed cat cracking of heavy oils. The reactors are so designed as to allow for continuous catalyst regeneration. Thermal cracking, which was an important process before the development of fluid catalytic cracking, is being phased out. Visbreaking and coking units are installed in a significant number of refineries, and their application is expected to increase.

Catalytic cracking, like thermal cracking, breaks heavy fractions (principally gas oils) into lighter fractions, and is the key process in the production of large volumes of high-octane gasoline stocks, furnace oils, and other useful middle distillates. The use of a catalyst permits operation at lower temperatures and pressures than those of thermal cracking and also inhibits the formation of undesirable by-products. Fluid catalytic cracking processes have, in most cases, replaced the fixed-bed and moving-bed processes which used a beaded or pelleted catalyst. The catalyst presently used in the process is primarily zeolite.

Hydrocracking is a catalytic method of converting refractory middle-boiling or heavy sour feedstocks into high-octane gasoline, reformer charge stock, jet fuel, and/or high grade fuel oil. This process has a high degree of flexibility in adjusting production to meet changing product demands. It is one of the most rapidly growing refinery processes. The types of catalysts commonly used are tungsten sulfide-silica alumina, iron-HF clay, nickel-silica alumina, and molecular sieves.

Coking is used to process the heavy asphaltic vacuum still residuals which do not pass into the cat cracking or lube oil operation after vacuum distillation. The coking operation involves destructive distillation of the very heavy low value residuum. Coking this material produces lighter materials by means of thermal cracking. The products of this operation include gas, naphtha, gas oils, and coke. Coke is the carbonaceous material remaining after the volatiles are removed.

The coking process occurs either in a semibatch operation called delayed coking or is performed continuously in a fluidized bed process. In the delayed coking, the feed is heated and pumped into large drums. The material is then cooled to remove the heat of reaction and is maintained at a fixed pressure which vaporizes the remaining volatile materials in the feed. When the drum is full, the process is stopped and the drum is opened. The coke is removed using hydraulic cutters.

In the fluidized bed process, the residum feed is heated and sprayed into a hot fluidized bed of coke. The coke particles grow and are removed from the system when their size exceeds the maximum size required for fluidization. Seed particles of smaller size are added continuously to the process to maintain the bed particle size distribution in the required operating range.

6.3 Upgrading Processes

Many products and by-products obtained from conversion steps undergo upgrading to generate a salable product which meets certain defined characteristics and increase the yield. Typical upgrading processes are alkylation, polymerization, reforming, isomerization, and drying/sweetening. The upgrading process used is dependent on feedstock and desired end product.

Alkylation is the addition of an isoparaffin (usually isobutane) to an olefin (propylene, butylene, etc.) in the presence of a catalyst to produce a high-octane alkylate, which is one of the most important components of automotive fuels. Sulfuric acid is the most widely used catalyst, although hydrofluoric acid and aluminum chloride are also used. Alkylation process capacity is expected to continue to increase with the demand for high-octane gasoline.

Polymerization converts olefin feedstocks (primarily propylene) into a higher molecular weight polymer gasoline. While polymerization yields, per unit of olefin feed, are less than alkylation yields, newer promoted cat cracker catalysts produce a feed that favors polymerization. Because of the higher ratio of olefins to isobutane produced, alkylation cannot convert all of the olefins to high-octane alkylate. Therefore, while only a few refineries currently use polymerization, its use may increase depending on the use of newer catalysts for cracking.

An example of a polymerization process is Dimersol, a process used to dimerize light olefins such as ethylene, propylene, and butylene (Anonymous 1984). The main applications of this process include dimerization of propylene to produce a high-octane low-boiling gasoline called Dimate, and the dimerization of n-butylene to produce C_8 olefins for plasticizer synthesis. Dimerization is achieved in a liquid phase at ambient temperature by means of a soluble catalytic complex. The catalyst is removed by a caustic wash process which generates an aqueous waste stream. After the catalyst is removed from the reaction mixture, the products are separated by means of distillation.

Reforming is a process of molecular rearrangement to convert low-octane feedstocks to high-octane gasoline blending stock, or to produce aromatics for petrochemical uses. The principal reactions are dehydrogenation, dehydrocyclization and isomerization. The undesired hydrocracking also occurs to a small degree. Multi-reactor, fixed-bed catalytic processes have completely replaced the older thermal processes. There are many variations, but the essential difference is the composition of the catalyst involved. The types of catalyst commonly used in this process are bimetallic platinum-rhenium and various combinations of group VIII elements.

Isomerization is another molecular rearrangement process which is very similar to reforming. The charge stocks generally are lighter and more specific (normal butane, pentane, and hexane). The catalysts used are platinum supported on alumina, or platinum supported on molecular sieves. The desired products are isobutane for alkylation feedstocks and high-octane isomers of the original feed materials for motor fuel.

Drying and sweetening are processes concerned primarily with removal of sulfur compounds, water, and other impurities, from gasoline, kerosene, jet fuels, domestic heating oils, and other middle distillate products. "Sweetening" is the removal from these products of hydrogen sulfide, mercaptans, and other sulfur compounds, which impart a foul odor and/or decrease the tetra-ethyl lead susceptibility of gasoline. Drying is accomplished by salt filters or adsorptive clay beds. Electric fields are sometimes used to facilitate separation of product from treating solution.

6.4 Offsites and Auxiliary Processes

In addition to the main process units, the refinery will have other processes or operations which support the overall primary process. These processes include gas recovery and treatment, sulfur recovery, hydrogen manufacturing, wastewater treatment, steam and cooling water utilities, and blending/packaging.

Gas recovery and treatment facilities are provided to sweeten and recover the light ends produced by the refining process. Typically, the light ends from the primary distillation operation and tail gas from hydrotreating and cat cracking will contain C_1 thru C_6 hydrocarbons, hydrogen sulfide, and water. This material can be upgraded to fuel gas and liquefied petroleum gas (LPG) in the gas plant. Typical operations include recovery of hydrocarbons via compression or lean-oil absorption, removal of hydrogen sulfide by amine scrubbing and then separation of the C_4 + hydrocarbons by distillation. The C_4 + hydrocarbons can also be converted to gasoline or used elsewhere in the refinery.

Hydrogen sulfide from amine units and from the sour water stripper (which treats nearly all aqueous process streams in the refinery), is then converted to elemental sulfur in a Claus plant. Conversion to elemental sulfur is obtained by burning part of the hydrogen sulfide to form sulfur dioxide. The sulfur dioxide is then reacted with hydrogen sulfide to form elemental sulfur and water vapor in a series of vapor phase

catalytic reactors. Tail gas containing sulfur and sulfur compounds from the Claus plant is further treated by Beavon or other processes before being released to the atmosphere. The ammonia present in the feed gas to the Claus plant is oxidized to nitrogen and water.

Hydrogen manufacturing is another auxiliary process. Some of the refinery hydrogen demand is satisfied by catalytic reforming, but not all. It is therefore necessary to manufacture hydrogen to meet the full process demand. The most common method of manufacture is by reacting methane (natural gas) with steam over a nickel catalyst. The products are hydrogen and carbon dioxide. Carbon dioxide is removed by amine scrubbing and a hydrogen product of about 95 to 98 percent purity is obtained.

The required utilities, which include electric power, steam, and cooling water are produced on site. Steam flows of up to 1000 tons per hour, at several pressure levels, are generated to provide process power and heat. The fuel source is gas, oil, or refinery byproducts. Electric power is purchased from utilities and supplemented by cogeneration or generation onsite where feasible (e.g. through FCC power recovery train). Cooling water is supplied as either once-through water or recirculated cooling tower water.

Blending is the final step in the production of finished petroleum products. Blending is required to meet quality specifications and market demands. The largest volume operation is the blending of various gasoline stocks, including alkylates and other high-octane components, with anti-knock (such as tetra-ethyl lead), anti-rust, anti-icing, and other additives. Diesel fuels, lube oils, waxes, and asphalts are other refinery products which normally require blending of various components and/or additives. Packaging at refineries is generally highly automated and restricted to high volume, consumer-oriented products such as motor oils.

7. WASTE DESCRIPTION

The primary specific wastes associated with petroleum refining, along with their process sources, are listed in Table 7-1. While these wastes have been classified into seven distinct groups (separation process wastes, conversion process wastes, upgrading process wastes, wastes from auxiliary processes, equipment cleaning wastes, waste-water treatment wastes, and waste from utilities production), many other more

Table 7-1 Petroleum Refining Process Wastes

No.	Waste Classification	Process Origin	Description	RCRA Code
1.	Separation process wastes	Kerosene or lube oil refining	Filter clays	--
2.	Conversion process wastes	Fluid catalytic cracker	Spent catalysts	--
		Hydrotreating, hydrocracking		--
3.	Upgrading process wastes	Alkylation, reforming, isomerization	Spent catalysts	--
		Alkylation	Acid sludge and lime	--
		Dimersol	Spent caustic	--
4.	Auxiliary process wastes	Amine scrubbing	Spent amine	--
		Stretford process	Spent Stretford solution	--
		Claus process, steam reforming, sulfuric acid plant	Spent catalysts	--
5.	Equipment cleaning wastes	Heat exchangers	Sludge	K050
		Crude storage tank bottoms	Sludge	--
		Leaded gasoline tank bottoms	Leaded sludge	K052
6.	Wastewater treatment wastes	API separator	Sludge	K051
		Dissolved air flotation	Oil, water	K048
		Slop oil tank	Sludge	K049
		Vacuum filter	Sludge	--
		Biological treatment	Sludge	--
		Storm water settling basins	Sludge	--
7.	Utility production wastes	Raw water treatment	Sludge	--
		Once-through cooling water	Sludge	--
		Cooling tower blowdown treatment	Sludge	--
		Boiler feedwater treatment	Sludge	--

detailed classifications are possible due to the diverse and complex nature of the industry. Additionally, the exclusion of RCRA codes from many of the waste streams only means that no specific "F" or "K" RCRA code exists.

7.1 Separation Process Wastes

Principal wastes associated with separation processes are spent filter clays used for lube oil and kerosene refining. Spent clay is produced in significantly greater quantities from the clay contacting process than from the fixed bed process. In a contacting process, the clay is mixed with the oil and subsequently removed with a rotary vacuum filter. Treatment with fixed bed clay is presently more predominant and is used to remove color, chemical treatment residues, and traces of moisture from product streams such as gasoline, kerosene, jet fuel, light fuel oil, and BTX (benzene-toluene-xylene) fraction from catalytic reformate. The spent clay from either of the above processes is usually disposed of in a landfill.

7.2 Conversion Process Wastes

Conversion process wastes originate from operation of the fluid catalytic cracker, hydrotreating operations, hydrocracking operations, and coking operations. Fluid catalytic cracker (FCC) catalyst is continously regenerated by burning off the coke formed on the catalyst during the cracking process. The flue gas from the regenerator passes through a series of cyclones that recover most of the catalyst. This recovered catalyst is then returned to the reactor vessel. Because of air pollution regulations, refineries have installed electrostatic precipitators or equivalent tertiary separation devices to significantly limit catalyst fines in the regenerator flue gas. These catalyst fines are either landfilled, or in some cases sold. They are generated on a continuous basis, but are generally disposed of on an intermittent basis.

A number of refinery processes require the use of a fixed-bed catalyst. These processes include catalytic reforming, hydrodesulfurization, hydrotreating, hydrocracking, and others. These catalysts become inactive (viz six months to three years) and are eventually replaced in the reactors with fresh catalyst during a unit shutdown. Many of these catalysts contain valuable metals which can be recovered economically. Some of these metals, such as platinum and palladium, represent the active catalytic component; other metals are contaminants in the feed which are deposited on the

catalyst during use (e.g. nickel and vanadium). After valuable metals are recovered (a service usually performed by the outside companies), the residuals are expected to be disposed of as solid waste.

The major contaminating metals found on catalytic cracking catalysts are vanadium, nickel, copper, chromium, and iron. Small amounts of these metals are present in the crude petroleum and, except for some of the iron, all are in the form of metal-organic compounds. Some of these compounds are volatile and when the vacuum gas oil feed to the catalytic cracking units is prepared, they appear in the gas oil. A fraction of the iron, and probably chromium, found on the catalyst is the result of erosion and corrosion either in the lines or equipment.

Coke which is produced in the course of fluid coking and delayed coking, is sold as solid industrial fuel or for use in electrode manufacturing. Coke fines are generated intermittently and their quantity is a function of handling techniques. A certain amount of spillage, and consequent contamination with dirt, results during the course of loading operations onto trucks and railroad cars.

7.3 Upgrading Process Wastes

Process wastes from upgrading operation include primarily sludges resulting from neutralization of acidic streams in alkylation process and spent dessicant clays. The residuals from other upgrading processes, such as reforming, isomerization, polymerization and sweetening include wastes resulting from spent catalyst re-processing (usually offsite), neutralized spent caustic from dimerization operation and spent salt or clay from drying.

Alkylation sludges from the HF alkylation process are produced as a result of removal of acid from organic streams (isobutane recycle and alkylate), vent scrubbing, tank sludge and HF regenerator bottoms (acid oils). The wastes from the sulfuric acid alkylation include residuals from acid regeneration (usually done by an offsite contractor), caustic washes and acid blowdown stream. Alkylation sludges are produced as a result of direct neutralization of acidic effluents using lime or indirectly by using lime to reconstitute primary base, such as KOH. The sludges are usually landfilled. Acid soluble oils from HF alkylation are either sold, burned or recycled to other units in the refinery.

7.4 Auxiliary Process Wastes

The amine scrubbing process, used to remove hydrogen sulfide and carbon dioxide from refinery gases, generates a spent amine waste stream. Another waste stream, which contains spent anthraquinone disulfonic acid (ADA) along with vanadium salts, results from the Stretford section of the Beavon process that removes hydrogen sulfide from the tail gases originating from a Claus plant. Both of these wastes are often drummed and disposed of in a landfill. The wastes from auxiliary processes also include spent catalyst from steam reforming, Claus plant, and sulfuric acid plant.

7.5 Equipment Cleaning Wastes

Equipment cleaning wastes are mainly generated from heat exchanger and storage tank cleaning. Heat exchanger bundles are periodically cleaned during plant or unit shutdown. Scale and sediment resulting from such cleaning is collected in sumps, from which it is either flushed into the process sewer system or shoveled out and disposed on land. The disposal practices for spent chemical cleaning solutions could not be ascertained. The heat exchanger cleaning waste is considered to be a RCRA hazardous waste.

Solid sediment from incoming crude oil accumulates at the bottom of the crude oil storage tanks. These tanks are cleaned periodically to remove the sediment. The cleaning frequency is dependent on the sediment content in the crude oil. In refineries which use mixers in the storage tanks, this waste source is non-existent. Constituents of the crude tank sludge vary with type of crude oil as well as with handling and shipping methods employed prior to delivery to the refinery. Settled sludge consists of a mixture of iron, rust, clay, sand, water, sediment, and occluded oil and wax. Usually, this mixture is a tightly held emulsion which does not separate on settling. The frequency of sludge removal varies from once a year to once every ten years.

Solids from leaded or non-leaded products settle to the bottom of storage tanks, where they remain until they are removed. This accumulated sludge is removed whenever the tank service is changed, the sediment content of the stored product exceeds specifications, or the tank itself needs inspection or repair. The characteristics of the deposited sludge will vary with the type of product stored in the tank. Leaded tank

bottoms are considered RCRA hazardous and special handling methods are used when the sludge is removed. It is removed at intervals varying between once a year and once every five to seven years. The sludge is spread on special concrete pads for weathering. Weathered sludge is disposed of in a Class I landfill.

7.6 Wastewater Treatment Wastes

Waste due to wastewater treatment is produced by the API separator, dissolved air flotation unit, slop oil tank, vacuum filter, biological treatment system (if present), and the stormwater settling basins. Solids which settle in the API separator during primary wastewater treatment are periodically removed with a vacuum truck, water is discharged to the secondary treatment and oil is recycled back to the crude unit through slop oil tank. Refinery API separators are usually connected to the oily water plant sewer. The bottoms, therefore, are a mixture of settleable portions of all sewered wastes, such as tank bottoms and desalter sludges, and, probably contain a certain amount of all other compounds that are present in the wastewater. These sludges are listed as RCRA hazardous wastes. In some refineries, additional oil and solids are removed from the API water effluent by dissolved air flotation. The flotation process takes place in a tank with or without the aid of chemicals. Air bubbles form and bring the finely divided solids and oil particles to the surface, where they are skimmed off. Oils are pumped to the slop oil tank. Sludge is sent to a landfill. The waste is classified as RCRA hazardous.

Skimmed oil from the API separators is usually pumped into a slop oil tank where the mixture is separated into three fractions: oil, water, and emulsion. The oil is returned for reprocessing, and the water is recycled back to the API separator. The emulsion layer may be disposed as a sludge, or it may be further treated, i.e., de-emulsified. De-emulsification is carried out by chemical or by physical treatment. The former process employs the use of special chemicals or agents, heat, and settling tanks. The later involves removal of suspended solids by centrifugation or vacuum filtration and the water and oils are separated in settling tanks. In either process, the oil is reprocessed, the water is returned to the wastewater treatment system, and the solids are disposed as a solid waste. This waste is classified as a RCRA hazardous waste.

In order to reduce sludge volume, some refineries concentrate certain waste streams through use of a common dewatering system. The dewatered cake from these

processes is disposed to land, while the filtrate or centrate is returned to the wastewater treatment system.

In the process of biological treatment of refinery aqueous waste streams emerging from the primary or secondary treatment, excess bio-sludge is created which, for efficient operation, must be controlled by wasting. The waste bio-sludge has a very high water content (99%) and is dewatered prior to disposal. This waste is generated intermittently at a rate which is dependent upon activated sludge process variations, the desired level of process efficiency, and the raw waste load.

Silt which collects in the stormwater settling basins in some refineries is periodically removed, de-watered, and land disposed. The quantity of silt is usually a function of the amount of rainfall and/or refinery paved area rather than of process complexity.

7.7 Utilities Production Wastes

Utility wastes are created by treatment of raw process water or once-through cooling water conditioning, cooling tower water blowdown treatment, cooling tower sludge, and boiler feedwater treatment. Raw water is usually strained, clarified using coagulation, flocculation, and sedimentation, and sometimes softened using lime treatment. Water pumped from a nearby source is passed through primary settling tanks prior to usage for once-through cooling. Sludge is periodically removed from these tanks.

The blowdown from the recirculating cooling water system is treated to precipitate chromium. Chromium salts are added to the cooling water to inhibit corrosion of carbon steel. Sludge which settles in the cooling tower basin is removed whenever the cooling tower is out of operation. It is either washed into the process sewer system or shoveled out and land disposed. This sludge also contains chromium.

Spent lime from cold or hot lime softening and from the clarification of boiler feed water is continuously discharged, de-watered in a settling basin, and disposed on land or re-used for neutralization of acidic waste streams (e.g. HF alkylation spent acid). The quantities and composition of the spent lime sludges are dependent upon the characteristics of the raw makeup water.

8. WASTE GENERATION RATES

In 1976, the EPA published a study on Hazardous Waste Practices in the petroleum refining industry (Jacobs 1976). One of the four basic objectives of the study was to determine the source, nature, and quantity of potentially hazardous wastes generated by industries engaged in the business of refining crude oil. Seventeen representative refineries were selected for study. Potential sources of hazardous waste were identified, sampled, and chemically analyzed for a range of constituents. These analyses served as the basis for estimates of total waste emissions from the refining industries. This information was subsequently reported in a 1979 study (Jacobs 1979). Generation rates are summarized in Table 8-1 for various petroleum refining waste streams. More recent waste generation data were not in evidence at the time of final report preparation.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

Generation and minimization of waste from petroleum refining can be initially viewed in the simple context of conceptualizing the complex process of refining as one in which the undesirable impurities naturally occurring in petroleum (principally heavy metals, water, sulfur, oxygen and nitrogen) are removed from the hydrocarbons. At this general level, it is important to note that the wastes produced due to impurity removal are unavoidable and can only be reduced by using lighter crude feedstock (an issue of high economic and political complexity) or by a decrease in the use of petroleum (an even more controversial and complex issue); neither one is suitable even for a topical exploration in this study. Hence, waste minimization in petroleum refining is more readily addressed in terms of what can be done given a current mix and flow of refinery feedstock. Here, the following general areas of focus are distinguished.

- Maximize utilization (minimize loss) of auxiliary materials and supplies. For example, extending the catalyst's life results in less frequent catalyst replacement thus reducing possible waste associated with its disposal or reprocessing.

Table 8-1 1974 Waste Generation Rates from the Petroleum Refining Industry

Waste	Oil (Weight %)	Water (Weight %)	Others (Weight %)	Total (Metric Tons/Yr/ 1,000 BPSD Crude Capacity)
Kerosene filter clays	3.5	5.0	91.5	1.0
Lube oil filter clays	21.9	50.0	28.1	431.2(a)
Neutralized alkylation sludge	6.9	54.2	38.9	47.4
Heat exchanger cleaning sludge	10.7	53.0	36.3	0.7
Crude oil tank bottoms	47.4	13.3	39.3	0.2
Leaded gas tank bottoms	20.0	0.3	79.7	0.8
API separator sludge	22.6	53.0	24.4	4.7
Slop oil emulsion solids	18.0	40.0	42.0	2.3
Biological treatment sludge	0.3	87.0	12.7	6.2
Storm water silt	3.9	25.0	71.1	2.7
Once through cooling water sludge	0.4	25.0	74.6	16.8
Cooling tower sludge	0.4	75.4	24.2	0.1
Boiler feedwater treatment sludge	0.3	59.0	40.7	70.5

Source: Alternatives for Hazardous Waste Management in the Petroleum Refining Industry (Jacobs 1979).

(a) Metric tons per 1,000 BPSD lube capacity.

- Search for less toxic substitutes. An example of less toxic materials substitution is found in the use of non-chromate corrosion inhibitors for cooling water treatment.

- Maximize slop oil recovery. This pertains to oil that is lost with sludge and emulsion solids leaving primary or secondary wastewater treatment. In this context, one should address the causes of slop oil generation and the ways to improve its separation efficiency from aqueous streams.

- Maximize energy and water conservation. This reduces waste generation associated with treatment of boiler feedwater, plant water, and cooling tower water.

- Reduce equipment cleaning frequency to cut down on equipment cleaning waste.

All of the above practices are encountered in one form or another at virtually every refinery. The attempt to identify and characterize waste minimization options is presented below. Most of the principal waste streams leaving a refinery were addressed -some of which are exempt from federal regulations (but not from state regulations), others that are not considered to be hazardous, and still others that are listed RCRA wastes. The rationale for including all streams was provided in the introduction to this appendix.

9.1 Description of Techniques

The list of individual primary waste streams along with a list of possible source reduction methods is presented in Table 9-1. Sections below deal with the description of the listed methods. All proposed methods appear to be technically feasible; however, the decision of whether or not to use a particular method is highly site specific and is dependent on other factors such as economics, cost/benefits, configuration of existing facility, and local regulatory constraints.

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures titled "good

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE PETROLEUM REFINING INDUSTRY

Waste Stream		Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
			Quantity	Quality						Probable	Maximum
Separation Process Filter Clays Only	1	Replace filtration with hydrotreating	1	1	3	1	3		0 0	1 7	1 7
	2	Regenerate and recycle clay	1	1	3	2	2		1 5	0 8	
	3	Use fixed bed clay filtration process	1	1	2	2	1		1 0	0 3	
		Overall	1 00	1 00	2 67	1 67	2 00	0 01	1 5	0 9	1 7
Conversion Process FCC Catalyst Only	1	Demetalize gas oil to cat cracker	0	0	3	1	2		0 8	1 1	1 1
	2	Minimize aeration and purge steam	0	0	2	3	1		1 5	0 1	
		Overall	0 00	0 00	2 50	2 00	1 50	unknown	1 5	0 6	1 1
Upgrading Process Alkylation Wastes Only	1	Proper operation of the process	2	2	3	3	1		2 3	0 2	
	2	Use KOH to neutralize HF acid waste	2	1	3	2	2		1 5	0 6	
	3	Upgrade feedstock by hydrogenation	1	2	3	1	2		0 8	1 1	1 1
		Overall	1 67	1 67	3 00	2 00	1 67	0 31	2 3	0 7	1 1
Auxiliary Process Spent Amine and Stretford Solutions	1	Choice of proper amine solution	2	2	3	3	1		2 3	0 2	
	2	Reduction of amine loss	2	2	3	2	3		1 5	1 1	1 1
	3	Prevent deterioration of Stret soln	1	2	2	2	1		1 0	0 3	
	4	Alternatives to 2,7-ADA	1	1	3	2	1		1 5	0 4	
	5	Recover products from the wastestream	1	2	1	1	1		0 3	0 2	
	6	Alternatives to Stretford process	1	2	2	2	2		1 0	0 5	
		Overall	1 33	1 83	2 33	2 00	1 50	unknown	2 3	0 4	1 1
Equipment Cleaning Heat Exchanger Sludge (*), Crude Oil Tank Bottoms, and Gasoline Tank Bottoms (*)	1	Decrease film temperature	1	1	2	1	1		0 5	0 4	
	2	Reduce deposit precursors in fluids	1	2	2	2	1		1 0	0 3	
	3	Use proper corrosion inhibitors	1	1	2	3	1		1 5	0 3	
	4	Use air coolers or electric heaters	0	0	2	2	1		1 0	0 1	
	5	Use smooth heat exchange tube surface	1	1	1	1	1		0 3	0 3	
	6	Reduction of Pb in gasoline	1	1	3	3	1		2 3	0 2	
	7	Install storage tank agitators	1	1	3	1	2		0 8	1 1	
	8	Use liners/corrosion resist material	0	0	2	1	1		0 5	0 4	
	9	Prevent oxidation of crude oil	1	1	1	3	1		0 8	0 1	
	10	Refine/recycle sludge for organics	1	1	3	1	3		0 8	1 7	1 7
		Overall	0 80	0 90	2 10	1 80	1 30	0 01	2 3	0 5	≈1 7

(*) These streams include listed "F" and/or "K" RCRA wastes

TABLE 9-1 continued

Waste Stream		Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
			Quantity	Quality						Probable	Maximum
Wastewater Treating	1	Segregate aqueous and oily wastes	1	1	2	3	1		1 5	0 1	
API Separator	2	Recover oil from API sludge	1	1	3	1	3		0 8	1 7	1 7
Sludge (*),	3	Install floating roof covers on unit	1	1	1	1	3		0 3	0 6	
DAF Float (*)	4	Use pressurized air in air flotation	1	1	1	2	2		0 5	0 3	
Slop Oil Tank	5	Oversize unit to max. sludge removal	0	0	1	2	1		0 5	0 1	
Sludge (*),	6	Optimize flocculant usage/addition	0	0	1	1	1		0 3	0 2	
Biosludge, and	7	Use alternate cleaning techniques	1	1	2	1	2		0 5	0 8	
Silt	8	Use sludge in the production of coke	1	1	4	1	2		1 0	1 5	
	9	Better operating practices	1	1	2	3	1		1 5	0 1	
		Overall	0 78	0 78	1 89	1 67	1 78	0 10	1 5	0 6	1 7
Utility Production	1	Install air coolers	0	0	3	3	1		2 3	0 2	
Raw Water	2	Heat exchanger tube leak prevention	0	0	2	2	2		1 0	0 5	
Treatment Sludge,	3	Proper cooling tower water treatment	2	2	2	3	1		1 5	0 1	
Cooling Tower	4	Minimize cooling tower duty	0	0	2	3	1		1 5	0 1	
Sludge,	5	Use cleaner make-up water	0	0	2	2	2		1 0	0 5	
CT Blowdown	6	Use non-chromate water treatment	2	2	3	1	2		0 8	1 1	1 1
Treatment Sludge,	7	Add insulation to pipes, tanks, ect	0	0	1	3	1		0 8	0 1	
and BFW Treatment	8	Convert steam to reboiled strippers	1	1	2	2	1		1 0	0 3	
	9	Maximize heat recovery	3	3	1	3	2		0 8	0 1	
	10	Better operating practice	2	2	2	2	2		1 0	0 5	
		Overall	1 00	1 00	2 00	2 40	1 50	0 57	2 3	0 4	1 1
All Sources		All Methods						1 00	2 2	0 5	1 2

(*) These streams include listed "F" and/or "K" RCRA wastes

operating practices" have also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practices:

- o Waste stream segregation
- o Personnel practices
  - -- management initiatives
  - -- employee training
- o Procedural measures
  - -- documentation
  - -- material handling and storage
  - -- material tracking and inventory control
  - -- scheduling
- o Loss prevention practices
  - -- spill prevention
  - -- preventive maintenance
  - -- emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Separation Process Wastes

These wastes include kerosene and lube oil filter clays. Some uses of clays inclusive final treating of lube oil base stocks to improve color and remove acidic compounds, copper removal from kerosene filtrate, and removal of BTX from catalytic reformate. The following methods allowing for elimination or reduction of this waste stream were noted:

- o Replace clay filtration with hydrotreating.
  Where a need to remove color bodies and olefins exists, hydrotreating is replacing clay filtration as the method of choice. Hydrotreating does a better job of improving color, increasing stability against oxidation, and has no yield loss (the oil measured in the spent filter clay represents a loss of some of the most valuable products produced in a refinery). It also eliminates the problem of spent clay disposal.

- Regenerate and recycle spent clay.

  Spent clays from the contact process may constitute one of the largest waste streams from major refineries. At least one refinery reported that it was attempting to recycle this clay (Jacobs 1979). It is not known what type of regeneration process was being used, but their previous attempts to regenerate contact clay by burning the residual oil with air, or by using roasting kilns or similar equipment, were not satisfactory. Close temperature control is necessary for the clay to maintain its activity, and with the variations in the amount of residual oil left on the clay, this becomes extremely difficult. The Socony-Mobil Oil Company has developed their Thermofor kiln for the regeneration of non-activated clay. The process consists of washing the spent clay with naphtha to free it from oil and render it mobile. It is then dried by steam heating and fed to the clay burning kiln where it is regenerated by controlled combustion of the absorbed impurities. The unit is quite complex and a considerable amount of auxiliary equipment is required. The process has been in use for many years on a batch basis, but has, as yet, never been run as a continuous operation.

- Use fixed bed clay filtration process.

  The fixed bed (percolation) process uses more clay for a given duty as compared to the fluid bed (contact) process but the spent clays can be regenerated many times using kiln. In addition, clays used in the fluid bed process must be treated with sulfuric acid before use. The main advantage of the fluid bed process, however, is that it has a neutralizing effect on acid treated oils.

9.1.2 Conversion Process Wastes

Conversion process wastes include spent catalysts from FCC, hydrotreating and hydrocracking. FCC catalyst is continuously regenerated by burning off the coke formed on the catalyst during the cracking process. Some of the metal compounds in the feed are adsorbed on the catalyst. In the catalytic cracking unit regenerator, where coke is burned off the spent catalyst, the organic portion of these molecules is burned off and the metals are oxidized to an inorganic oxide that remains on the

catalyst. Corrosion and erosion products may be mixed with the catalyst as fine particles or may also be deposited on the catalyst surface. The heavy metals, vanadium and nickel, and to a lesser extent, iron and copper, act as dehydrogenation catalysts and produce excessive quantities of undesirable coke and light gases (especially hydrogen). In many cases, these metal contaminants are the primary reason for discarding part of the equilibrium catalyst. Fresh (uncontaminated) catalyst is then added to maintain a desirable level of contamination.

The flue gas from the regenerator passes through a series of cyclones that recover most of the catalyst which is returned to the reactor vessel. Fines are recovered in electrostatic precipitators. Operators try to control the operation such that the fines production rate about equals the poisoning rate in order to avoid removal of equilibrium catalyst. Suggestions for reducing FCC catalyst losses are as follows:

- Demetalize gas oil charged to cat cracker.
  Catalyst withdrawal rate can be reduced by decreasing the rate of catalyst deactivation by removal of metals before gas oil is charged to the reactor. A mild hydrogenation or hydrotreating process has been used on the catalytic cracking feed in some units. This feed treatment removes some of the metal compounds and provides other benefits to the catalytic cracking operation, such as removing sulfur, which reduces the amount of sulfur emissions from the regenerator, and increasing yields of desirable products such as gasoline.

- Minimize use of aeration and purge steam.
  Excess fines will be generated by overuse of aeration and steam purges during cracker operation.

Minimization of spent catalysts from hydrotreating and hydrocracking operation was not addressed in detail. Generally, catalyst losses can be reduced by proper loading and pre-sulfiding procedures, good reactor temperature control, good flow distribution and continuation of research into development of more active, stable and selective catalysts.

9.1.3 Upgrading Process Wastes

The principal wastes of concern are the sludges resulting from neutralization of acidic effluents from alkylation operation. Wastes associated with the alkylation process primarily result from carryover of acid into the organic phase (oil) and carryover of organic phase into acid. The carryover in both directions is attributed to physical entrainment (physical carryover) or to the formation of undesirable compounds between components of the organic phase and the acids (chemical carryover). The following methods were noted as potentially useful in reducing alkylation wastes:

- o Proper operation of the process.
  By reducing the degree of physical and chemical carryover that occurs, a reduction in caustic waste can be achieved. Physical carryover of acid can be caused by using excessively cold acid, improper acid settler level, low reactor pressure, and an excessive acid recycle rate. Chemical acid carryover can be due to low isobutane or acid concentration, high reaction temperature, and improper mixing. Improvements in operation of the alkylation process were previously discussed in more detail (NPRA 1977, Libberman 1980, Hammershaimb and Shah 1985).

- o Use KOH to neutralize HF acid waste.
  In the past, lime was used to neutralize acid carryover and other wastes produced by the alkylation process directly. The newer process alternative relies on potassium hydroxide (KOH) to neutralize acid; this is followed by reconstitution of KOH by reacting KF with lime outside of the neutralizer or scrubber. With HF alkylation, the switch to KOH for initial neutralization has achieved a reduction in the overall amount of lime required and, thus, in the amount of sludge produced. Additionally, the overall system efficiency and reliability is improved over calcium or sodium based solutions (Hammershaimb and Shah 1985).

- o Upgrade feedstock by selective hydrogeneration or hydroisomerization.
  Because of increased demands for higher octane gasoline and the increased conversion of heavier crudes to lighter products, there has been a relative decrease in the quality of alkylation feed throughout the industry

(Hammershaimb and Shah 1985). By selectively hydrogenating diolefins (acid polymer precursors) in the feed, acid consuming impurities can be removed and hence overall acid consumption reduced. Hydroisomerization processes are commercially available, e.g. HPNIVB process.

9.1.4 Auxiliary Process Wastes

Refinery gases that contain CO_2, H_2S, and traces of COS and CS_2, are typically scrubbed by amines to remove these components. The amines form certain non-regenerable compounds which must be removed by intermittent bleed of amine inventory. The following source control methods were noted:

- Choice of proper scrubbing solution.
  Presently, monoethanol amine (MEA), diethanol amine (DEA), diglycolamine (DGA), diisopropanolamine (DIPA), and methyldiethanolamine (MDEA) are in use. There are some advantages and disadvantages associated with any of these solvents. Typically, the waste generation aspect is addressed in terms of reducing costly amine losses due to formation of non-regenerable compounds. This aspect usually receives close attention of a process designer. The ultimate choice of solvent depends on specific application, therefore it is difficult to generalize which solvent is most preferable from the waste generation standpoint. Recently MDEA has been more frequently applied than in the past. The use of non-amine gas treatment processes (e.g. Purisol, Selexol or Benfield) should be carefully considered from the waste generation aspect as an alternative to amines.

- Reduction of amine loss.
  The loss of amine solution through degradation can lead to many problems. Besides the actual loss of solution, degradation products are corrosive and can lead to equipment fouling. Studies have shown that the rate of DEA degradation increases with increasing temperature and pressure (Melsen and Kennard 1982). Therefore, the rate of DEA flowing through the regenerator reboiler should be kept high and the steam or gas temperature kept low so as to lower the film temperature on the process side. Efforts

to remove the degradation products by means of carbon filtration have not been very successful (while the appearance of the DEA improves from dark brown to light yellow, no major degradation products were removed). Also, increased pressure was shown to accelerate degradation process. Examination of tradeoff's between higher amine losses and operating the regenerator at atmospheric pressure with amine gas re-compression appears worthy of consideration.

The use of additives to inhibit amine deterioration is in common use and was found effective in the case of "Amine Guard", an additive manufactured by Union Carbide.

Tail gases from the Claus sulfur recovery plant are treated to remove residual sulfur and its compounds (CS_2, COS, SO_2, H_2S) in order to meet sulfur emission standards. Among the processes used to treat the tail gases is the Beavon process which relies on a catalytic reactor to convert all sulfur compounds to H_2S and a Stretford section where H_2S is selectively scrubbed and oxidized to sulfur in an aqueous phase. To avoid excessive buildup of non-regenerable impurities (chiefly thiosulfate), the Stretford solution inventory is bled, thus generating a potentially hazardous waste stream containing sodium salts of anthraquinone disulfonic acid (ADA), vanadium compounds, sodium bisulfite, thiosulfate, carbonate, and bicarbonate. The following techniques are considered useful to minimization of this waste stream.

- Prevent excessive deterioration of Stretford solution.

  If the absorber is overloaded with inlet tail gas, excessive amounts of thiosulfate and insoluble vanadium oxysulfide are formed. When a Claus plant produces big swings in the sulfur content of the tail gas, overloading of Stretford solution is likely, which in turn leads to excessive chemical losses. Adding small quantities of sodium tartarate to the solution helps prevent the formation of vanadium oxysulfide and hence reduces losses (Kohn and Riesenfeld 1979). The initial degradation of 2,7-ADA during startup can be inhibited by adding sodium thiosulfate to virgin solution prior to startup.

- Alternatives to 2,7-ADA.

  Since 2,7-ADA is not very stable, the use of more stable substitutes is desireable. Proprietary formulations, such as "Elvada" and "Amada", have been offered as possible substitutes. Elvada contains a mercury catalyst and thus may not be an environmentally advantageous substitute. Amada does not contain mercury and appears to be a better choice.

- Recover products from the waste stream.

  Two processes, one developed by Nittetsu Chemical Engineering Ltd. (Japan) and the other by Peabody-Holmes Ltd., are available to recover useful products from Stretford process wastes (Kohl and Riesenfeld 1979). Both processes concentrate the waste stream by evaporation of water, followed by combustion of the residue under reducing conditions, where vanadium, sodium carbonate, and hydrogen sulfide are recovered to be returned to the process. Organic compounds, such as ADA and other additives, are destroyed in the combustion process. These processes are thus capable of reducing wastes from the Stretford process.

- Alternatives to Stretford process.

  An alternate process (Selectox) for sulfur recovery from Claus tailgas was developed and licensed by Ralph M. Parsons Co. and Union Oil Co. (Beavon et. al. 1979). This sulfur removal process uses a cobalt-molybdenum catalyst to hydrolyze and hydrogenate COS, CS_2, SO_2, and elemental sulfur to H_2S which is then catalyticaly oxidized to SO_2 using air. The H_2S and SO_2 then form elemental sulfur by the Claus reaction. Since no chemicals other than the catalyst are used in the process, no solution purges are necessary. The process is said to have lower capital investment and produce a slightly better quality sulfur than the Stretford process. At least one industrial unit (Wintershall AG, Lingen, West Germany) has been reported to use this process. New promising developments include Unocal's Unisulf process which is yet to be tested on commercial scale.

Minimization of spent catalyst wastes from the Claus plant, sulfuric acid plant and steam reformer was not addressed.

9.1.5 Equipment Cleaning Wastes

Heat exchanger tube bundle cleaning sludge is a major contributor to equipment cleaning wastes. Often these wastes are discharged into a pit which is then flushed out with water. This sludge/water waste flows into the chemical or oily water sewer (OWS) and on into the API separator for primary treatment. The following suggestions for waste reduction were noted:

- Decrease film temperature and increase turbulence on heat transfer surfaces.
  A decrease in film (or surface) temperature and an increase in turbulence (or velocity) will decrease the asymptotic fouling resistance, thus reducing the cleaning frequency. This could be accomplished by not oversizing the heat exchangers excessively or by provision of recirculation of cooling fluid in order to maintain high velocity (Garrett-Price 1985). On the cooling water side, excessive film temperatures often result from low flows of cooling water during turndown operations. Where possible, the feasibility of temperature control using process stream bypass as opposed to direct throttling of cooling water should be addressed.

- Reduce deposit precursors in process fluids and cooling water.
  Calcium and magnesium salts present in crude oil contribute to scale buildup and corrosion in crude preheat trains. Reducing the allowable salt content by water injection upstream of desalters, operating the crude desalters at maximum efficiency, and addition of emulsifier downstream of desalter will minimize the exposure of the process side of the exchanger to scale forming salts (Van der Wee and Tritsmans 1966). If economically feasible to do so, a softened water (i.e., clarified boiler blowdown) can be used as cooling tower makeup. The reduced level of calcium and magnesium salts in cooling water would reduce the exposure of the tubes to scale forming salts.

- Use proper corrosion inhibitors in cooling water.
  Selection of the proper type and dosage of corrosion inhibitors will cut down on scale formation. Typical corrosion inhibitors currently being used include chromium, zinc, phosphates, and free chlorine (USEPA 1978). Since

these additives pose a potential pollution problem, they need to be removed prior to discharge or their use avoided. The use of organic chelating agents as replacements for zinc and chromium compounds is a viable alternative (Gesick 1974, Zecher 1975). The use of a reacted phosphate product developed by Hercules, Inc., as a substitute for heavy metal inhibitors has been reported (Wilkes and Hodel 1984). Wites Chemical Co., reports the use of a non-oxidizing biocide as a similar substitute (Hoblack and Kawlor 1985). A proprietary nonchromate treatment, Dianodic II, was found to be effective in controlling scale formation at National Cooperative Refinery Association, McPherson, Kansas (Nichols et al. 1980).

- Substitute air coolers or electric heaters for heat exchanger.
  Reduction in sludge generation due to bundle cleaning on utility side can be accomplished by replacing heat exchangers with air coolers or electric heaters. This should be done if economically sound.

- Use smooth heat exchanger tube surfaces or on-stream cleaning devices.
  Providing a smooth surface for heat transfer will minimize the sites available for scale formation to start. The use of electropolished stainless steel tubes in a black liquor forced circulation evaporator (paper and pulp industry) resulted in a drastic reduction in cleaning frequency from once-a-week to once-a-year (Uddeholm Co., Tubec Tubes Brochure). Smooth non-stick surfaces can also be provided by Teflon*. Complete Teflon exchanger designs are available (Dupont 1985). The additional advantage of Teflon tubes is their ease of cleaning and corrosion resistance.

  The onstream cleaning devices generally rely on an insert propelled by the process fluid through the heat exchanger tube. Brushes propelled back and forth by flow reversal accomplished with a diverter (Water Services of American Inc.) or sponge balls recirculated by a special retrieval/reinjection device (Amertap Inc.) are both commercially available onstream cleaning systems.

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* Registered trademark of E.I. DuPont de Nemours & Co.

Sludge due to cleaning of crude oil, leaded gasoline, non-leaded gasoline, and other product storage tanks is another major equipment cleaning waste. The following methods for reducing the generation of sludge were noted:

- Reduction of lead in gasoline.
  The current trend of reducing the level of lead in gasoline, coupled with the possibility of a ban on leaded gasoline, will lower the toxicity of leaded gasoline tank sludges.

- Install storage tank agitators on crude oil tanks.
  Agitation of the vessel contents will prevent the deposit of settleable solids and hence reduce the need for cleaning. It must be noted that agitation does not by itself reduce the amount of waste generated; it simply transfers the solids downstream to the crude unit - they eventually end-up either in asphalt or coke.

- Use corrosion resistant materials.
  Some of the sludge generated is the result of corrosion or deterioration of the storage tank internals. Installation of a liner or using materials of construction which are more resistant to the corrosive elements of crude oil will reduce sludge production.

- Prevent oxidation of crude oil.
  Gums and resins form as the result of air oxidizing unsaturated compounds in the crude oil. Air oxidation can be minimized in crude storage tanks by providing a nitrogen blanket over the surface of the oil or, more commonly, by use of floating roofs. The floating roof should preferably be of the double cover type with liquid seals. Many storage tanks are already equipped with floating roofs as a result of air emission regulations.

- Refine or recycle sludge for organic content.
  Conventional cleaning of crude tanks often relies on mechanical removal of sludge and its subsequent land disposal. The use of warm oil and circulating cleaning techniques reduces the ultimate sludge volume and allows for recovery of considerable quantities of valuable crude tied up in the sludge (Barnett 1980). Here, a light gas oil, clean crude stock, or other

available low viscosity straight run distillate is warmed, mixed with dispersant additive, and circulated through the tank. This process re-suspends the sludge and dissolves the crude that is entrapped in the sludge, which amounts to 60 to 90 percent of oil by volume. The liquid can then be sent to the refinery's slop oil recovery system. Again, as in case of agitation, the solids are transfered to the part of the process where they can be more efficiently separated from valuable entrained liquid.

The sludge volume can be reduced at small refineries by using the Victor extraction process (API-NPRA Conference 1980). Here, the sludge is dumped into a container and agitated for an extended period of time with steam and air. This process separates the residual oil trapped in the sludge which can then be taken off from the top of the container. The solids, significantly smaller in volume by comparison to the original sludge, settle to the bottom. This process works well for granular type sludges but is not very effective for clay type sludges.

At large refineries, the sludge volume can be reduced by concentrating it using vacuum, gravity belt, or automated plate and frame filters (centrifugal filters were not found to be very effective). Also, the sludge volume can be reduced significantly by using patented Chevron Recovered Oil Process. This process is said to be more effective than conventional filtration methods (API-NPRA Conference 1980). Other methods involve thermal/chemical emulsion breakup using steam or indirect heating. One such method was used at Vickers Petroleum refinery where the de-emulsifier was added to the sludge, which was then pumped through a steam heater into a conical bottom decanter (op. cit.). Other techniques include ultrasonic de-emulsification, solvent extraction (e.g. using B.E.S.T. process available from Resources Conservation Co.), and recently patented electroacoustic dewatering (Battelle 1985).

9.1.6 Wastewater Treatment Wastes

Oily aqueous wastes which originate in the refinery are collected in chemical or oily-water sewers (OWS) which usually discharge to an API separator. The feed to the

separator can vary widely in both flowrate and composition. The wastes are usually comingled and consist of oil, water, suspended solids, and various emulsions. The function of the separator is to perform the initial separation of solids from liquids and oil from water. Virtually all dilute aqueous wastes from the refinery will pass through the API separator.

Skimmed oil from the API separators is usually pumped to the slop oil tank where the mixture is separated into three phases: oil, water, and emulsion. The oil is returned for reprocessing, and the water is recycled to the API separator. The emulsion may be disposed as a waste or may be processed further for recovery of oil.

Dissolved air flotation (DAF) units are usually installed after the API separator. Water which is discharged from the API separator contains emulsified oil, water, and suspended solids. Suspended solids are removed in the DAF unit either by flocculating agents and settling, or by air coming out of solution and carrying the particles to the surface along with the oil. The froth "float" which contains emulsified oil, water, and solids is skimmed off and sent to a de-emulsifier.

Basically, the problem of reducing API sludge volume can be approached in two ways:

- Reduce the raw waste loads upstream of the API separator.

- Maximize recovery of oil from the sludge before disposal.

Raw oil-containing wastes entering the API separator can originate from heat exchanger cleaning operations, crude tank cleaning operations, equipment and piping drainage and steamouts prior to maintenance, maintenance parts cleaning, and spill cleanup. Generally, most methods mentioned in Section 9.1.5 apply. Continuous sources of aqueous streams entering the API separator include sour water stripper, desalter, boiler blowdown, cooling tower blowdown, BFW treatment (ion-exchange regeneration brine) effluent, and other refinery units. Source control techniques allowing for a decrease in the carryover of oil are addressed in the appropriate sections. Methods proposed for reducing waste associated with waste water treatment are as follows:

- Reduce API separator inflow by waste segregation.
  A major portion of the API separator load is water that originally may or may not have been an oily waste. Efforts should be made to install a separate sewer system which would convey oil-free aqueous wastes. Boiler blowdown, some pump seal water, ion exchanger regeneration brines, and other non-oil containing wastes should be diverted to this system. These streams would then by-pass the API separator, thereby reducing its load and thus improve separation efficiency in the existing separators.

- Recover oil from API sludge.
  Most techniques discussed in Section 9.1.5 under "refining or recycling of sludge for organic content" for crude tank sludges also apply to API sludge. These methods include filtering, thermal/chemical emulsion breakup and, possibly, ultrasonic separation of oil from solids. Solvent extraction was found to have high effectiveness and application potential (API comments).

- Install floating roof covers on API separators.
  At Conoco Inc., installation of floating covers on API separators was found to reduce the oxidation of oil that results in the formation of heavy waste material (API-NPRA Conference 1980). Floating roofs were installed originally to reduce air emissions.

- Use pressurized air technology.
  DAF units using pressurized air generate less than one half of the float volume compared to induced air units for a given amount of solids removal. New facilities should incorporate this technology in the design if technically and economically compatible with the overall refinery plan. Facilities currently using induced air systems should convert to pressurized air systems if the economics justify this change-over.

- Use sufficient overdesign factor for new systems.
  With oversized systems, the impact of process upsets and flow excursions will be minimized. Reducing the impact of process upsets and flow excursions leads to much more efficient and reliable operation of the individual waste treatment units.

- Use proper flocculants.
  Proper matching of flocculant to refinery waste will increase the separation efficiency of the process and reduce the amount of waste that is carried downstream.

- Use alternate cleaning techniques.
  All of the methods that reduce waste due to equipment cleaning (Section 9.1.5) will reduce waste associated with wastewater treatment. Additionally, removal of sludge prior to its discharge to API separator may reduce organic carryover into water and reduce the resulting biosludge. An example is an alternate design of a heat exchanger bundle cleanup pit to recirculate water through filter to remove sludge prior to discharge into API separator (NMERDI 1985).

- Use sludge in the production of coke.
  For facilities with cokers, most of the sludge produced by the API separator, the DAF unit, and the slop oil tank can be injected into the coker and converted to coke (API comments).

- Better operating practices.
  These include minimization of spills of process fluids and reduction of the practice of hosing refinery wastes into the chemical sewer. Because spent filter clays have high oil adsorption qualities it makes them ideally suited for use on in-plant oil spills. The clays are typically from the filtration of light-end distillates and lube oils. Rather than immediately disposing of this spent clay, the refineries stockpile them within the diked areas around the refinery until used. Stockpiling of the clay also allows the hydrocarbons to degrade by microbial action. For additional methods, the reader is refered to a separate study of "good operating practices" contained in this appendix (Study #B19).

9.1.7 Utility Production Wastes

Sludge that settles in the cooling tower basin is removed whenever the cooling tower is out of operation. It is either washed into the process sewer system or shoveled out and

disposed to a landfill. The sludge sources are residues from cooling tower biocides, hardness scale from exchanger surfaces, cross contamination from process fluids, biological materials, and airborne dirt. Suggestions for sludge volume reduction are as follows:

- o Install air coolers.
  Replacing water-cooled exchangers, where practical, with air fan coolers will reduce contamination of cooling water with process fluid as well as the volume of cooling water in circulation.

- o Heat exchanger tube leak prevention.
  Cross contamination from the process side of heat transfer equipment is one of the sources of sludge creating materials. Part of this cross contamination is created by leaky exchanger tubes. Use of seal welded tube joints in some cases, or double tubesheets will minimize or eliminate process fluid leakage into the cooling water (and vice-versa). Tube vibration analysis should be performed more routinely in the design stage.

- o Proper cooling tower water treatment.
  Cooling tower chemicals are responsible for sludge buildup. Operators should refrain from overtreatment to avoid excess buildup due to chemical addition. The heavy metal content in the cooling tower sludge can be reduced or eliminated by methods such as the nonchromate treatment discussed in section 9.1.5.

The cooling tower blowdown treatment sludge can be minimized by the following methods:

- o Minimize cooling tower duty
  This is closely related to energy conservation in the refinery. The waste (low pressure) stream, e.g. from leaky steam traps, is condensed using cooling water which increases cooling tower duty. Reducing steam consumption helps to reduce cooling tower blowdown.

- o Use of a cleaner make-up water
  This will reduce the blowdown stream and, thus, the toxic sludge generated by chromate removal. Use of boiler blowdown as a make-up stream should be considered.

- Use of non-chromate treatment
  As mentioned in Section 9.1.5, this will reduce the toxicity of the sludge produced by treating the cooling tower blowdown. The non-chromate corrosion inhibitors are reliable, except in services where water film temperatures are very high - in such cases the design, operation, and controls of exchanger should be carefully re-examined anyhow.

Most refineries use a vast amount of steam in normal operation. Feedwater to the boilers, particularly the high pressure boilers, must be very clean for safety reasons as well as equipment longevity. Any projects undertaken by the refinery which would seek to cut steam consumption would not only reduce spent lime production, but also result in operating cost savings. Some suggestions for reducing steam consumption are as follows:

- Add insulation to pipes, tanks, valves, etc.
  Decreasing heat losses from pipes, tanks, valves and other process units will reduce steam consumption. This, in turn, will reduce the load on the boiler feedwater treatment system.

- Convert steam strippers to reboiled strippers.
  All stripping steam eventually winds up in the waste treatment system. By converting to reboiled strippers where possible, the spent lime required in the treatment of the water used to produce stripping steam as well as the wastewater load to API separator will be eliminated.

- Maximize heat recovery from process streams.
  Identify those areas in the refinery for installation of additional heat exchanger networks to make maximum use of available heat energy.

- Better operating practices.
  Many refineries have areas where steam demand may be reduced. It is to the advantage of the refiner to promote the identification of areas and develop projects to increase the overall plant thermal efficiency. Promote an aggressive approach to steam system preventive maintenance. Maintain steam traps, valves and piping runs to minimize steam or condensate leaks. Provide strict guidelines to limit unneeded blowdown of boilers or

automate it. Provide rigorous maintenance of the condensate return systems and boiler feedwater treatment systems to minimize contaminants which enter into the boiler feedwater.

9.2 Implementation Profile

Good operating practices, while easy to implement, do not appear to have as high an impact on waste minimization as do process modifications, such as replacement of clay filtration with hydrotreating or recovery of oil from sludges. Process modifications are expected to be considered in the planning stages for unit replacement, major overhaul, or during the conceptual design stage for any new grass-roots facility. Considerable amount of engineering and economic analysis is usually required before a decision can be made because of the high capital costs involved.

9.3 Summary

The ratings of every listed method shown in the table were based on review of available literature, engineering judgement and input from the American Petroleum Institute. Each method was rated on a scale of zero to four for its effectiveness, extent of current use and future application potential. The current and future extents of waste reduction were then derived using the methodology presented in the introduction to this appendix.

A current reduction index of 2.2 (55 percent) is indicative of the significant level to which the noted wastes have already been minimized (CRI is a measure of the reduction of waste that would have been generated if none of the methods were practiced at their current level of application). By implementing additional waste reduction measures, or by increasing the use of existing measures, the amount of waste currently being generated can be reduced to a moderate extent, as evidenced by a future reduction index of 0.5 to 1.2 (12 to 30 percent).

The most effective measures currently applied to control hazardous (RCRA listed) wastes include segregation of aqueous and oily wastes, oil recovery from sludges, reuse of sludge as a coker feedstock and better operating practices.

The most effective future methods for minimizing hazardous wastes are those characterized by high individual FRI value. These include oil recovery from sludges and use of sludge as a coker feedstock.

10. PRODUCT SUBSTITUTION ALTERNATIVES

At this time there are no economic substitutes for petroleum products. Alternative sources of energy such as solar, nuclear, coal or shale oil cannot currently compete with petroleum to satisfy the energy needs at the level required in the United States. Until the world supplies of crude oil are exhausted, or oil becomes unavailable for other reasons, it is unlikely that it will be economically feasible for the alternatives discussed above to significantly displace the refining of crude oil in the near future.

One area in which product substitution has been occurring is with the product gasoline. Currently, there have been major efforts being undertaken to reduce and eventually eliminate the use of lead in gasoline. Producing a non-leaded gasoline requires additional processing to ensure the same level of octane as in leaded gasoline. Most commonly, alkylation is employed to boost octane levels so that more acid wastes are expected to be produced per gallon of gasoline sold. Offsetting this increase however, is the elimination of wastes due to tetra-ethyl lead production, leaded gasoline storage tank sludge, and the emission of lead into the environment by way of combustion. Eliminating the use of lead in gasoline is expected to achieve a large reduction in the amount of toxic metal contained in a refineries waste.

Another alternative which is worth mentioning is methanol which can be produced from petroleum and which can be successfully used in place of gasoline (Othmer 1985). Cited environmental advantages include low fire hazard, absence of carcinogenic BTX compounds present in unleaded gasoline, and very low exhaust emissions of hydrocarbons, carbon monoxide, nitrogen oxides and aldehydes.

11. CONCLUSIONS

While the petroleum refining industry has significantly reduced its waste volume generation, it appears that further reduction is possible. Our estimates indicate that it may be technically feasible to further reduce the volumes in the range of 12 to 30

percent. However, any further voluntary reduction will only be realized from in-plant studies which show that changes, such as the ones suggested in this report, are economical.

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13. INDUSTRY CONTACTS

P.J. Tussey, American Petroleum Institute, Washington, D.C.

1. PROCESS: PHENOLIC RESINS MANUFACTURE
2. SIC CODE: 2821(8)
3. INDUSTRY DESCRIPTION

Manufacturers of phenolic resins are included as part of the plastic materials and resins industry. Large phenolic resin producers tend to produce the resins for sale to other users. Smaller producers tend to produce resins for captive use.

3.1 Company Size Distribution

Relative to many other chemical producing industries, the phenolic resin manufacturing industry contains a large number of producers. This may be because the manufacturing processes involved are not highly capital intensive and because of the large variety of final products.

In 1980, there were 50 companies producing phenolic resins at 102 establishments. Of the 50 companies, 6 produced more than 100 million pounds of phenolic resins during the year, 14 produced between 10 and 100 million pounds, and 31 produced less than 10 million pounds. Each establishment produced an average of 30 million pounds of phenolic resins in 1980. The employment figures by EPA regions for the phenolic resin industry were not available.

3.2 Principal Producers

The following principal producers manufacture in excess of 100 million pounds of phenolic resins annually:

Borden Incorporated	Occidental Petroleum Corporation
Georgia-Pacific Corporation	Owens-Corning Fiberglass Corporation
Monsanto Company	Reichhold Chemicals Corporation

3.3 Geographical Distribution

Table 3-1 displays the number of phenolic resin manufacturing establishments by EPA Region. Region V contains 28 establishments, or over 25 percent of the establishments in the U.S. However, relative to other chemical manufacturing industries, the phenolic resins industry is geographically widespread. Figure 3-1 displays the geographical distribution of phenolic resin facilities located in the U.S.

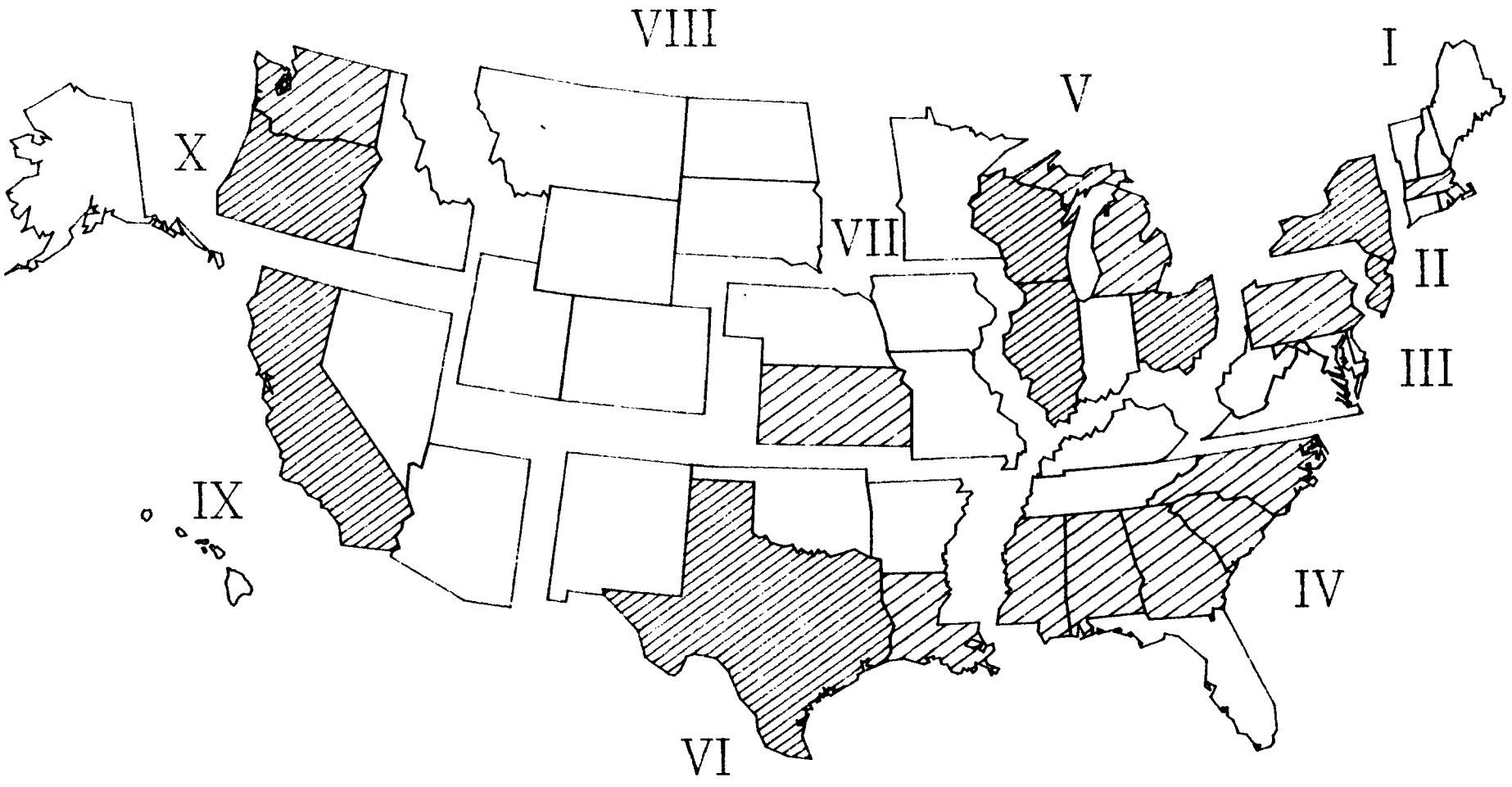
Table 3-1 Geographical Distribution of Phenolic Resins Manufacturing Establishments by EPA Region

EPA Region	Number of Establishments
I	5
II	14
III	5
IV	15
V	28
VI	10
VII	3
VIII	1
IX	6
X	15
National	102

4. PRODUCTS AND THEIR USE

The binding quality of phenolic resins make them very versatile. Thus, they are used in a wide variety of products including:

Molding Compounds	Plywood
Insulation	Fibrous or Granulated Wood
Foundry Binders	Laminates



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Roman numerals show EPA regions

Figure 3-1 Phenolic Resins Plants in the U.S.

Brake Linings	Clutch Facings
Abrasives	Rubber
Protective Coatings	

For 1985, phenolic resin production was estimated to be 2.5 billion pounds (Greek 1985). Table 4-1 gives the use pattern for phenolic resins.

Table 4-1 1985 Use Pattern of Phenolic Resins

Use	Consumption
Bonding plywood and wood fiber board	60%
Other adhesives	28%
Molded items	10%
All others	2%

Source: Chemical and Engineering News (Greek 1985).

5. RAW MATERIALS

Reactants — Formaldehyde (solution or solid), phenol, calcium hydroxide, sulfuric acid, paraformaldehyde, hexamethyl tetramine, sodium hydroxide, substituted phenols.

Solvents — Cellosolve acetate, butanol, ethanol, methyl ethyl ketone, cyclohexanone, xylene.

Additives — Wood flour, amino resins, oils, plasticizers.

6. PROCESS DESCRIPTION

Phenolic resins are a broad variety of materials, all of which are based upon the reaction between phenol, or a substituted phenol, such as cresol or resorcinol, and an aldehyde, such as formaldehyde or acetaldehyde. Most significant resins are based upon the reaction of phenol with formaldehyde. By proper control of the reaction, a wide variety of phenol-formaldehyde resins can be manufactured.

In general, phenolic resins are produced batchwise in a batch kettle arrangement schematically depicted in Figure 6-1. The batch reactor typically has a size varying from 2,000 to 10,000 gallons. The reactor is equipped with a jacket to facilitate cooling or heating at different phases of reaction. The following sections deal with the manufacture of two principal types of phenolic resins: Resols and Novolacs.

6.1 Manufacture of Resols

Resols are thermoset phenolic resins used for making bonding resins, varnishes, or thermosetting molding powders. Resols are formed by the condensation of phenol and formaldehyde present in a molecular ratio of 1.0:1.5. An alkali, such as sodium hydroxide, is used as a catalyst.

Phenol, in molten form, is charged to the kettle followed by addition of 37 percent formaldehyde solution which washes away any residual phenol present in the lines leading to the kettle. After the catalyst is charged to the reactor, the reactor contents are heated to about 140°F by steam to start the condensation reaction. Once initiated, the reaction generates heat, which is removed by the water-cooled kettle jacket and a water-cooled overhead condenser. These are used to maintain the temperature at 140-175°F for 1 to 5 hours, depending on the required properties of the final product. The reaction is stopped at the desired point by cooling the reactor contents to 95°F. At this point, the caustic may be neutralized by the addition of sulfuric acid. The reactor contents are then heated to remove water and other volatiles from the resin. The removed water contains unreacted phenol, formaldehyde, and low molecular weight resins. This stream can be processed in a variety of ways

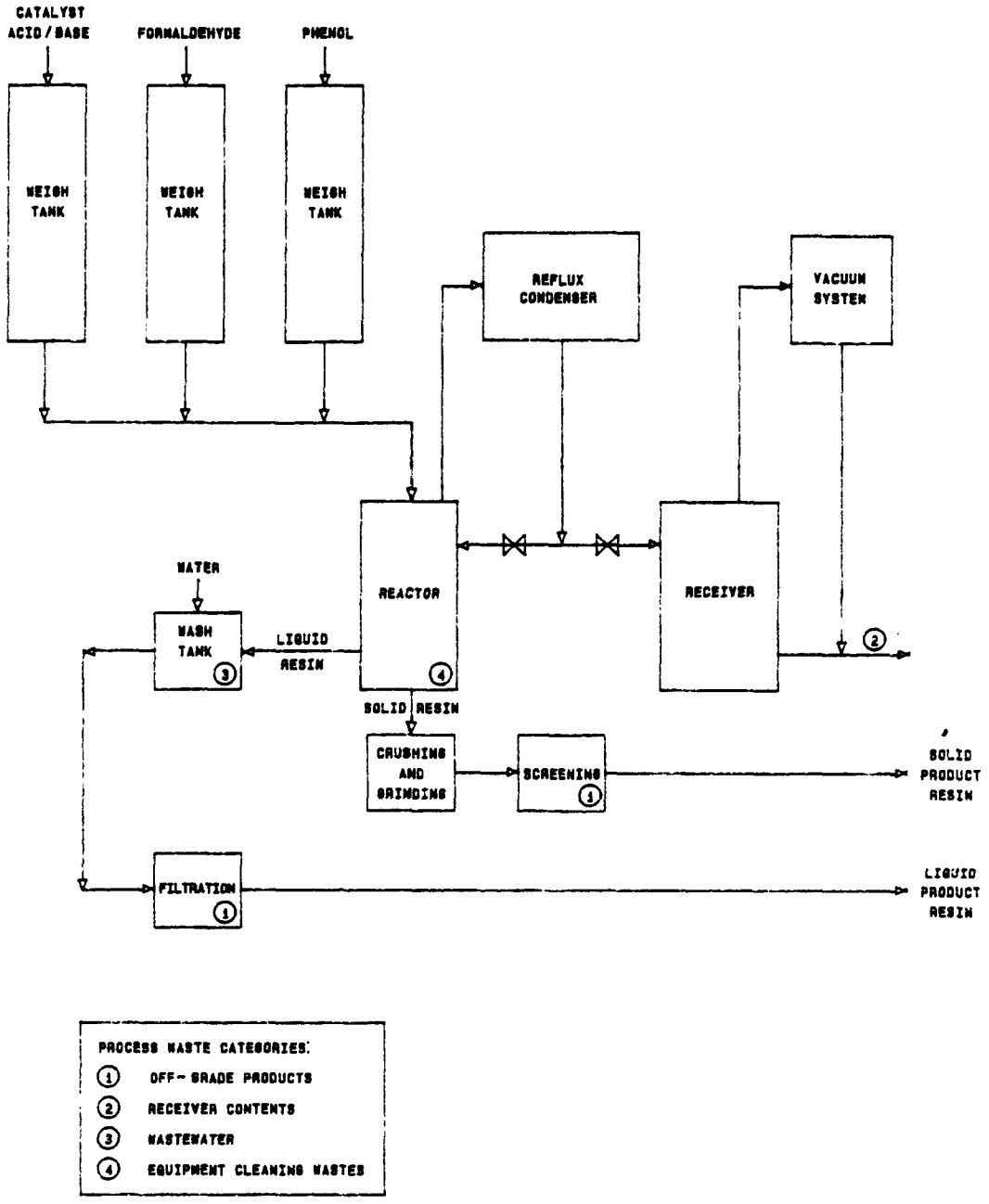

Figure 6-1 Process Flow Diagram for the Manufacture of Phenolic Resins

including re-use in compatible batches, phenol recovery followed by treatment, dilution followed by treatment, incineration and land disposal.

The product resin may be washed several times, resulting in a waste water stream. The solid products are dried and ground to a specific size prior to packaging. The liquid products are filtered prior to packaging. This filtration produces a solid waste of oversize resin particles which is disposed of by landfill or incineration.

By proper control of the reaction, three classes of products can be produced. If the reaction is stopped when the polymer is still water-soluble, the product can be used for bonding resins. If the reaction proceeds till the polymer precipitates, the product can be used to manufacture a varnish. If the reaction is carried out till the resin reaches the brittle stage, "one-stage" solid resin is produced and can be used as molding powder. In the last case, the molten resin must be quickly discharged in order to prevent solidification in the reactor.

6.2 Manufacture of Novolacs

The manufacture of Novolacs is similar to that of resols except that an acid such as sulfuric acid is used as a catalyst. The ratio of phenol to formaldehyde is normally 1.0:0.75-0.9. The deficiency of formaldehyde produces a stable, low molecular weight, thermoplastic.

Vapors generated by the heat of reaction are condensed and returned to the reactor in order to maintain the reaction temperature at 185-195°F. After 3 to 6 hours of reaction, the condensate is sent to a receiver instead of being returned to the reactor. When the temperature rises to 250-300°F, vacuum is applied to remove water and unreacted phenol. At this point, the receiver contains water, phenol, formaldehyde and methanol, which is used as a stabilizer for formaldehyde. This stream can be processed in a variety of ways including re-use in compatible batches, phenol recovery followed by treatment, dilution followed by treatment, incineration and land disposal.

The reactor contents need not be cooled as the polymerization is complete. The final product is purified by dehydration under vacuum before being dumped on cooling pans.

The reactors are periodically cleaned with caustic solution, generating an additional waste stream.

7. WASTE DESCRIPTION

Table 7-1 shows the primary waste streams associated with the manufacture of phenolic resins. The off-grade products, which amount to 0.8 percent of total resin production (Snell 1978), are the result of bad batches. This waste stream contains unreacted phenols, formaldehyde, methanol, and resins at various degrees of polymerization. This waste may be drummed and landfilled or stored onsite in concrete-lined lagoons. The material can also be incinerated using a fluid-bed combustor (Lanouette 1977).

Losses from grinding, screening, packaging, and filtering are routinely collected and reworked at most of the facilities. In a few cases, these handling losses generate a waste stream which is disposed of along with the off-grade products.

The liquid in the condensate receiver amounts to 67 percent of total resin production (Snell 1978). However, according to more recent information, this stream constitutes 30 percent of total resin production*. The stream is generated from product dehydration in the case of resols, or in the case of Novolacs, the water is removed in the final phase of reaction to accelerate polycondensation. This stream contains water, phenol, formaldehyde, methanol, and low molecular weight resins. The stream may be land disposed or may undergo recovery of phenol (hence producing a less toxic and more easily treatable wastestream), controlled incineration, chemical or biological oxidative treatment.

A wastewater stream, which amounts to 8 percent of total resin production (Snell 1978), is also generated when the final resin product is washed to remove traces of the unreacted phenol, formaldehyde, and salts produced by neutralization of the reaction mixture. This stream is usually filtered to remove any solids and then discharged to the sewer, or combined with the receiver effluents, or treated separately using chemical or biological oxidation, depending on the final organics content.

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*Reichhold Chemicals Inc. 1985: Private communication.

Table 7-1 Phenolic Resins Manufacturing Wastes

No.	Waste Description	Process Origin	Composition	RCRA Codes
1.	Off-grade products	Grinding, screening and packaging. Filtration of the liquid resin	Unreacted phenols, low molecular weight resins	---
2.	Receiver contents	Reaction water with organics	5-7 wt.% phenol 5-8 wt.% formaldehyde 5-7 wt.% methanol	---
3.	Wash water waste	Washing and/or neutralization of the product resin	Unreacted phenol and salts	---
4.	Spills	Reactor, storage tanks, valves, pumps	Phenol and formaldehyde, etc.	---
5.	Equipment cleaning waste	Washing Novolak reactor	Na_2SO_4 and NaOH in water	---

Spills and leaks are inadvertent discharges occurring at various plant locations. The liquid discharges are usually mixed with the receiver contents for disposal. It is expected that the waste resulting from spills and leaks will be small.

A caustic solution is used to wash the reactor for the manufacture of novolacs, generating a waste stream. This stream contains sodium sulfate, sodium hydroxide, and traces of phenol and formaldehyde in water. A similar, but acidic waste stream from resol manufacture is mixed with the receiver contents and disposed of as described previously.

8. WASTE GENERATION RATES

The recent nationwide waste generation rates from phenolic resins manufacturing process were not in evidence at the time of final document preparation. The most recent estimates found through literature search give fractional waste generation rates for 1974 (Snell 1978). Since the phenolic resin industry has made many process improvements in the last decade, the current waste generation figures are expected to be much lower than the 1974 figures. The 1974 estimates correspond to about 0.6 pounds of waste per pound of product, whereas current waste generation is estimated at less than 0.2 pounds of waste per pound of product*. The relative waste generation rates expressed as weight fractions of the total waste stream were computed based upon the 1974 data (Snell 1978) and other available, more current information. These relative rates are given in Table 8-1 and also in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

The summary of all the waste streams together with source reduction methods is shown in Table 9-1. The discussion of each method is given below along with the rationale for its inclusion and application cases, if known.

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* Reichhold Chemicals 1985: Private communication.

Table 8-1 Fractional Waste Generation Rates from Phenolic Resins Manufacturing

Waste	Percent of Total[a] (excludes added water)	Percent of Total[b] (includes added water)
Off-grade Products	1	> 1
Receiver Contents	64	10
Resin Wash-water	15	36
Spills	1	> 1
Equipment cleaning wastes	19	52
Total	100	100

Source: estimated by project staff.

(a) Water used for resin wash and equipment cleaning is excluded; only the organics and salts present in these streams are counted.

(b) Includes water added for resin wash and equipment cleaning.

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel practices
  - management initiatives
  - employee training
- o Procedural measures
  - documentation
  - material handling and storage
  - material tracking and inventory control
  - scheduling
- o Loss prevention practices
  - spill prevention
  - preventive manintenance
  - emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Off-Grade Products

Off-grade products containing traces of unreacted phenol and formaldehyde are obtained from bad batches and are usually landfilled offsite or stored on-site in concrete lined lagoons. The following source reduction methods were noted:

- o Proper control of reactor temperature.
  In most cases, bad batches are the result of the reactor contents being cooled too rapidly. This leads to the formation of an insoluble, infusible mass. This can be prevented by proper control of the reactor temperature, along with prompt attention to any rapid decreases in temperature. Temperature excursions can be minimized by:

- Frequent calibration checks of temperature sensors, and more frequent maintenance of temperature control systems.
- Frequent monitoring of set point drift.
- Use of reactors with separate jackets or coils for cooling water and steam. Such reactors are commercially available and will avoid the deposition of dissolved cooling water solids on the heat transfer surfaces when steam is applied. Buildup of these deposits leads to inefficient heat transfer and subsequently poor temperature control.

o Increased automation.

Bad batches may also result from failure to charge proper quantities of various reactants. This can be prevented by double-checking the quantity of input materials to the reactor. Usually, feed materials are weighed before being sent to the reactor. Weighing errors can be decreased by using an automated batching system properly maintained by frequent calibration. If installation of automated batching controls proves impractical, manual batching can be improved by closer supervision, better documentation procedures, better operator training, and frequent checks of weighing equipment.

o Re-use of off-grade products.

Off-specification products can sometimes be blended with high-grade product to yield an intermediate-grade resin which meets the required specification. This practice is not always possible; however, it appears to be widely used in the industry.

9.1.2 Receiver Contents

In resols manufacture, water is removed from the reactor to favor the poly-condensation reaction. This water stream carries phenol, formaldehyde, and other soluble organics and is stored in drums for land disposal, or treated to recover phenol.

In Novolaks manufacture, the reactor contents are maintained at constant temperature in the initial phases by condensing water vapor and returning the condensate to the kettle. Late in the reaction, the slowing polymerization rate is

increased by diverting the condensate to a receiver rather than to the reactor. The receiver contents are sent to waste storage. The following source reduction techniques were noted:

- Use of improved catalyst.

  The phenol and formaldehyde content in the receiver effluent can be minimized by obtaining higher conversion yields for the polycondensation reaction. This can be facilitated by use of more active catalysts (Brode 1982). One patented catalyst which is a combination of a divalent metal and an acidic material, is an alternative to presently used catalysts (Culbertson 1978). The use of improved catalysts should be examined for their environmental advantages along with their potential ability to reduce waste through better yields.

- Lower water content in the reactor.

  A patented process for high molecular weight Ortho Novolaks using exotherm control allows the use of higher concentration of aqueous formaldehyde (Culberston 1978). In this process, 50 weight percent formaldehyde can be used as opposed to 37 weight percent formaldehyde used in conventional processes (Brode 1982). The lower water content in the reactor should subsequently produce a smaller aqueous waste stream and also should improve reactant's conversion. This process is claimed to have an improved reaction rate because of less water and easier temperature control.

- Use of azeotropic solvents.

  Since phenol and water are totally miscible under reaction conditions, the water which is removed carries phenol with it. Use of an azeotropic solvent, such as xylene, can decrease the phenol content in water (Culberston 1978, Brode 1982). As water is continually removed, the organic phenol-rich phase can be separated and recycled. The environmental advantages and disadvantages of this suggested technique will have to be fully assessed, since introduction of entrainer or azeotropic solvent, such as xylene, may not always be desirable.

- Re-evaluation of current temperature trajectory.

  As explained earlier, in the final stage of reaction, water is removed from the reactor to promote the equilibrium shift toward novolac products. In the first stage of reaction, a vacuum reflux is used to maintain the reactor at 185-195°F. After 3-6 hours of reaction time, the condensate from the overhead condenser is sent to a receiver instead of being returned to the reactor. This switch-over point is crucial from the standpoint of phenol/formaldehyde losses through the overhead vapor. If this switch-over is made too early, the losses of organic reactants will be high because of their higher concentration in the reactor.

  In addition to the cost of lost reactants, another factor to be considered in the optimization is the cost of disposal and treatment of liquid waste. If the organics content in the liquid is more than 12%, the fuel requirements for incineration are minimal and phenol recovery by solvent extraction is less costly. If the organics content is lower, then solvent extraction becomes costly and the fuel requirements to support incineration may be substantial (Snell 1978).

  It is suggested that reassessment of the currently used temperature trajectory may lead to the overall lowering of waste generation rates in certain cases.

- Re-evaluation of reactant and/or catalyst addition strategy.

  Addition of reactants (phenol and/or formaldehyde) or catalyst (sodium hydroxide, sulfuric acid) can be done in one step, in increments, or continuously following a schedule designed for maximum conversion and minimum losses during the evaporative mode of reactor operation. Development of such a strategy can be assisted using a reactor modeling approach. For example, staged addition of remaining formaldehyde before switching to an evaporative mode from isothermal operation, reduces the free phenol content in the reactor, which reduces phenol losses through the vapor stream. As before, it is suggested that reconsideration of the reactant or catalyst addition strategy may lead to the overall decrease of waste generation in certain cases.

- Inversion of dispersion mode.

  The process involves a primary reaction cycle under basic conditions at 194-220°F and a secondary reaction cycle, at 176-194°F under neutral conditons in the presence of a protective colloid used to stabilize the dispersion (Brode 1982, Brode et al. 1974, Harding 1977). In the primary cycle, condensation of formaldehyde and phenol occurs. In the secondary cycle, inversion from a water-in-phenolic dispersion to a phenolic-in-water dispersion takes place speeding up the poly-condensation to the desired end point. Based upon preliminary review, the process seems to offer a potential for higher conversion and thus lower waste loads compared to the more conventional route.

- Internal phenol recycle with treatment of receiver contents.

  Recovery of phenols from aqueous streams and its recycle to the process has been practiced. Phenol separation from water can be achieved by several liquid solvent-extraction processes (Brode 1982, Lanouette 1977), adsorption processes, or critical fluid extraction. A discussion of these processes follows:

  The benzene-caustic phenolization process uses benzene as the extraction solvent in a packed tower with countercurrent flow. The caustic is used to wash the phenols from benzene, converting them to sodium phenolates. Using steam, carbonic acid, and additional caustic, phenols can be separated from the aqueous phase to be recycled to the process. Removal efficiency of 92-93% can be achieved. In some plants, it has been shown that the removal efficiency can be improved to 95% by using a Podbielniak centrifugal countercurrent solvent extractor instead of a packed column. Efficiencies of 98.6-98.8% can be achieved by using a pulsed packed column which improves scrubbing.

  The Lurgi Phenosolvan process uses isopropyl ether as the solvent in a multi-stage solvent extractor. This solvent has a lower boiling point than phenol and can be distilled from phenol for further reuse. The Ifawol dephenolization process uses a countercurrent packed column with a solvent that has a boiling point higher than that of phenol and is practically

insoluble in water. The phenol can be recovered from the dewatered solvent by vacuum distillation. After passing through a separator, the solvent can be recovered for reuse.

Activated carbon adsorbent, in the form of granules, has a finite capacity for removing phenol from waste water. Phenol can be removed from activated carbon by chemical regeneration (Lanouette 1977). The waste stream has to be filtered prior to contact with activated carbon. The disadvantage of this process is that carbon removes other organics present in the waste stream, thus the regenerated stream may contain other organics besides phenol. In addition to carbon, some polymeric adsorbents are found to be effective in removing phenol from aqueous waste (Fox 1975, 1978). The phenolic waste stream is passed through one or more polymeric adsorbent columns yielding an effluent containing less than 1 ppm phenol. Column loadings of 0.6 to 11 lbs of phenol per cubic foot of this adsorbent are possible at raw waste phenol concentrations of 100 to 50,000 ppm, respectively. Regeneration of the resin with concentrated formaldehyde allows convenient recycle of the resulting phenol formaldehyde eluate directly to the polymerization reactor.

A critical fluid extraction method for recovering phenol from waste water is commercially available*. The method uses a condensed gas, such as carbon dioxide in the vicinity of its critical point. Critical fluids have highly favorable solvent properties and they behave as a liquid in dissolving significant amounts of organic substance. At the same time, they behave like gases in that the rate of extraction is extraordinarily high compared to normal liquid solvents. Commercial systems are available for capacities ranging from 1 to 100 gallons per minute.

Each of the methods listed above has to be individually evaluated for a specific application. General environmental attributes of each method were not evaluated.

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* Critical Fluid Systems Inc. 1985: Personal communication.

- Altering resin molecular weight distribution and functionality to reduce wastes.

  Phenolic resins have different molecular weight distributions depending on their end use. By making small changes in their molecular weight distributions, the change in their properties may not be significant, but could contribute toward waste reduction (Brode 1982). By increasing the conversion slightly, the quantity of unreacted phenol and formaldehyde can be decreased. Though this does not result in lowering the quantity of waste water generated, it reduces the toxicity of this stream.

- Use of excess formaldehyde to reduce free phenol content.

  Free phenol content in the reactor can be decreased by using higher quantity of formaldehyde feed to the reactor. Excess formaldehyde can be removed from the resin by stripping. Lower free phenol results in lower phenol in the waste water stream, reducing its toxicity.

- Isolating the wash-water stream from receiver contents.

  The wash water is sometimes mixed with the receiver contents before treatment. If the wash water contains only traces of phenol, mixing it with the receiver contents results in a larger and more dilute waste stream. By isolating the wash water and treating it separately, the receiver contents will not be diluted. This could facilitate their disposal by incineration or use of phenol recovery options.

9.1.3 Resin Wash Water

In the manufacture of liquid resols, the final product may be washed with water several times to remove inorganic salts and traces of unreacted phenol and formaldehyde. This washwater is usually filtered to remove any solids present prior to discharge to the sewer or treatment as a separate stream or in combination with other aqueous streams. The following source reduction methods were considered for this waste stream:

- Use of counter-current washing.

  The amount of wash water necessary to remove a certain amount of unreacted phenol or formaldehyde is lowest when counter-current washing

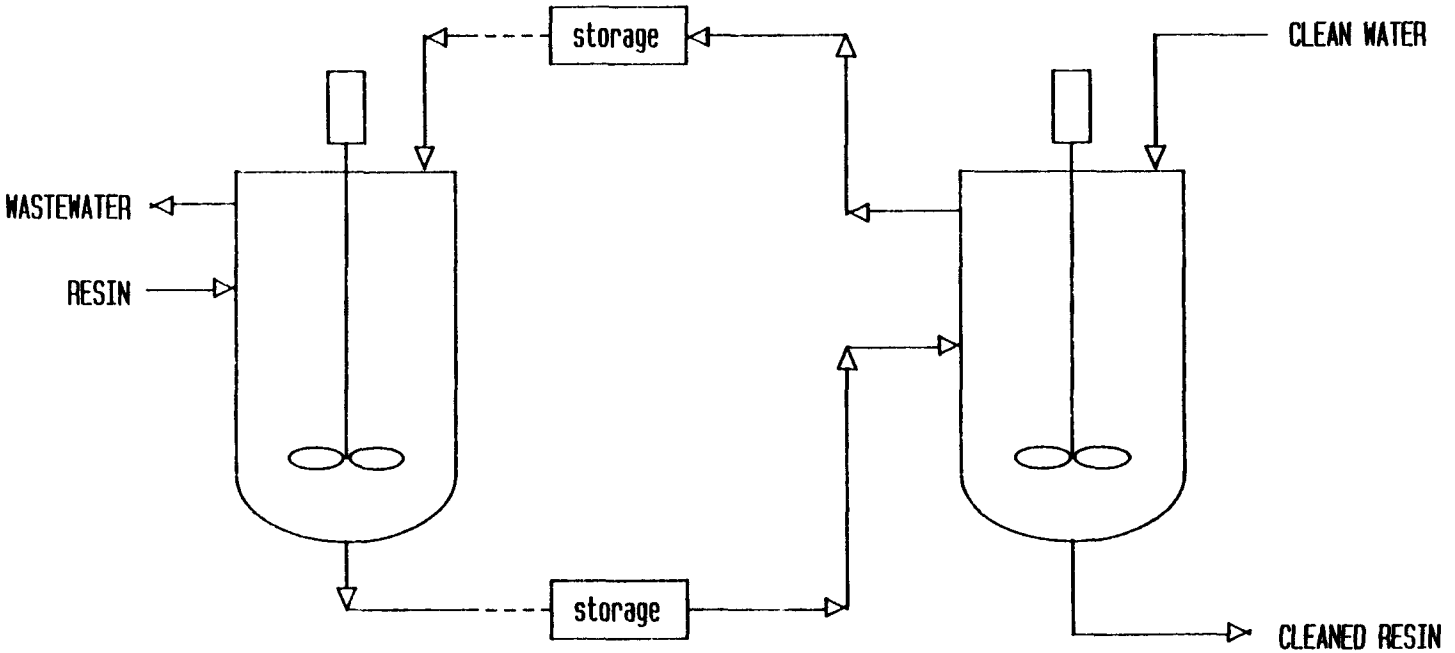

Figure 9-1 Illustration of Counter-Current Washing Concept for Batch Operation

is used. Counter-current washing may be more favorable in a continuous operation where washing can be done in counter-current extractors (e.g. rotating disk type) if the viscosity of the liquid resin permits such an operation. In batch operation, the liquid resin could be allowed to accumulate in tanks and counter-current washing can be done periodically.

When the product resin needs to be washed several times, counter-current washing (e.g. similar to the scheme shown in Figure 9-1) will generate low quantities of waste water. Counter-current rinsing may offer a substantial improvement over sequential rinse-decant sequences used to achieve the same washing efficiency. It is possible that due to the increased concentration of organics in the wash-water stream, it may then be suitable for phenol recovery.

- Re-use of resin wash water.

  The purpose of washing the resin with water is to remove inorganic salts and residual water-soluble organics. In priciple, it is possible to re-use the wash-water until the dissolved impurity concentration reaches prohibitive levels. This type of wash-water re-use is common in the synthetic rubber industry where the inhibitors present in monomers are washed using a caustic solution (Snell 1978). If wash-water is reused for the first rinse, the second (or consecutive) rinsing may require clean water to efficiently remove the contaminants. The wash-water accumulated from the first rinse may eventually be treated along with receiver contents to recover phenol.

9.1.4 Spills and Leaks

Spills are due to accidental discharges of liquids during transfer operations or equipment leaks. The spill cleanup wastes are stored in drums and are considered hazardous. Only the implementation of better operating practices is suggested for this waste stream, especially in the area of better operator training and preventive maintenance.

9.1.5 Equipment Cleaning Wastes

After each batch, the reactors for resols and novolacs are cleaned with dilute acid or caustic solution to remove resin particles that remain on the reactor walls. This intermittent waste stream is filtered to remove the particles and the filtrate is mixed with the receiver contents prior to disposal. The filtered particles are often mixed with other non-recyclable off-grade products and disposed of in a landfill. The equipment cleaning waste generated by the washing procedure contains traces of phenol and formaldehyde. On occassions, it is necessary to use solvent for equipment cleaning. In such cases, the resulting waste is generally incinerated, however, it may be landfilled by facilities which do not use an incinerator. The following source reduction techniques have a potential for reducing the amount of aqueous waste produced:

- Reduction of resin buildup on the reactor walls.
  The use of Teflon* coated reactors or reactors equipped with wipers that continually clean the walls will reduce polymer buildup on the walls. Teflon is known to possess low adhesion characteristics which may help to relieve buildup and help drainage. It is also suitable for use in process environments at temperatures up to 400°F which adequately covers the range involved in production of phenolic resins. Teflon coating must be closely scrutinized if there is an occasional need for mechanical cleaning that involves chipping off accumulated material. However, the use of Teflon may eliminate the need for mechanical cleaning altogether. The designs of double shaft mixers equipped with wall and bottom wipers are commercially available and are routinely used in applications requiring mixing of high viscosity resins.

- More complete drainage of process lines.
  Prior to rinsing with water, the equipment, along with process lines should be properly drained. Such drainage can be accomplished by proper piping layout (e.g. no pockets, sloping toward equipment) and also by "pigging" the lines, which is an encountered practice in the paint manufacturing industry. There, a plastic slug is propelled by an inert gas through the lines which

* Registered trademark of E.I. du Pont de Nemours & Co.

cleans them while increasing product yield. For phenolic resin process piping it may be possible to use a similar approach.

- Maximizing equipment dedication.

  The frequency of equipment cleaning can be reduced by maximizing equipment dedication to a single formulation. In the limit, a total dedication is accomplished by conversion from batch to a continuous process. Continuous processes for the production of phenolic resins have been developed (Euleco 1975, Anon. 1965). Since the market calls for a large diversity of products, it appears unlikely that these processes can be used universally. Proper production scheduling, e.g., maximizing the size of the product obtained from a single campaign, or scheduling compatible batch campaigns adjacent to each other is probably a much more widely practiced technique to lower the cleaning frequency and the associated waste.

- Filter resin recovery.

  Prior to shipping, liquid resins are usually filtered. The resin remaining in the filter casing can be easily recovered by blowing the resin out with the use of plant air prior to screen cleanup. This procedure was effectively used by Borden Chemical Company (Huisingh et. al. 1985).

- Use of a two step rinse with recycle of the first rinse.

  Some facilities use a "fill-and-empty" reactor cleaning technique, where the reactor is filled with water, which is subsequently dumped after agitation. This produces a large amount of wastewater contaminated with phenolic resins. As an alternative, an initial low-volume rinse (e.g. employing spray nozzles) can remove the bulk of the resins to produce a small quanity of wastewater with a high concentration of phenol. This material can be reused in the next compatible batch of resin. The tank can then be washed with a full volume rinse to generate a waste with a much lower resin content. This procedure, used at Borden Chemical Co., contributed to a 93 percent reduction in the amount of discharged organics (Huisingh et. al. 1985).

9.2 Implementation Profile

While some of the methods proposed or identified require installation of additional equipment, substantial reductions can be made through changes in operating procedures. The use of a two step rinse method with the recycle of the first rinse, and an increased awareness of waste on the part of plant personnel, contributed to a significant reduction in the organics lost with equipment cleaning wastes at Borden Chemicals Co. The procedure appears easy to implement at many phenolic resin manufacturing facilities.

The use of countercurrent product washing and the recovery of phenol from aqueous wastes for recycling to the process usually requires installation of additional equipment. These options may not be implementable at all facilities. Recovery of phenol using polymeric adsorbents or solvent extraction techniques was found feasible by some manufacturers.

Because different manufacturers produce different grades of resin, great variation in wastestream composition is encountered. Each facility must therefore choose the control measures compatible with its own specific requirements. For facilities already having suitable waste treatment plants or incinerators, many of the proposed methods cannot be economically justified. Implementation will ultimately depend on economic feasibility, which should take into account avoided treatment costs, avoided disposal costs for treatment residuals, and raw material savings.

9.3 Summary

The summary of all noted source control techniques is given in Table 9-1. Each technique was rated for its effectiveness, extent of current use, and future application potential on scale of 0 to 4. The ratings were derived by project staff based on review of the available data. The estimates of current level of waste reduction achieved (current reduction index) and possible future reduction (future reduction index) were obtained from the ratings in accordance with the methodology presented in the introduction to this appendix. Fractional waste generation rates (including water) were taken from Table 8-1. Current reduction and future reduction indices were also

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE PHENOLIC RESINS MANUFACTURING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Off-Grade Products	1. Proper control reactor temperature	1	1	3	3	1		2.3	0 2	
	2. Increase use of automation	1	1	3	2	2		1.5	0.8	0.8
	3. Re-use in product	1	2	3	3	1		2.3	0.2	
	Overall	1 00	1.33	3.00	2.67	1.33	0.01	2.3	0.4	0.8
Receiver Contents	1. Use improved catalyst	1	1	2	2	2		1.0	0.5	
	2. Lower water content in the reactor	1	1	1	1	1		0.3	0.2	
	3. Use of azeotropic solvents	1	1	2	1	2		0.5	0.8	
	4. Re-evaluate temperature trajectory	1	1	1	3	1		0.8	0.1	
	5 Re-evaluate react/cat addition method	1	1	1	3	1		0.8	0.1	
	6 Inversion of dispersion mode	1	2	2	1	1		0.5	0.4	
	7. Internal phenol recycle	2	2	3	2	3		1.5	1.1	1.1
	8 Alteration of resins molecular weight	1	1	2	2	1		1.0	0.3	
	9. Use excess formaldehyde	1	1	1	2	1		0.5	0.1	
	10. Isolate washwater from rec. contents	1	1	2	3	1		1.5	0.1	
	Overall	1.10	1.20	1.70	2.00	1.40	0.10	1.5	0.4	1.1
Resin Wash Water	1. Use counter-current rinse	1	1	3	1	1		0.8	0.6	0.6
	2. Re-use of resin wash water	1	1	2	0	1		0.0	0.5	
	Overall	1.00	1.00	2.50	0.50	1.00	0.36	0.8	0.5	0.6
Spills and Leaks	1. Better operating practices	1	1	2	3	3		1.5	0.4	0.4
	Overall	1.00	1.00	2.00	3.00	3.00	0.01	1.5	0.4	0.4
Equipment Cleaning Wastes	1. Reduce resin build-up on reactor wall	1	1	2	1	2		0.5	0.8	
	2. Use of a two-step rinse with recycle	1	2	3	1	3		0.8	1.7	1.7
	3. Maximize equipment dedication	1	1	3	3	3		2.3	0.6	
	4. Filter resin for recovery	1	1	2	1	3		0.5	1.1	
	5. More complete drainage/process lines	1	1	2	2	2		1 0	0.5	
	Overall	1.00	1.20	2.40	1.60	2.60	0.52	2.3	0 9	1.7
All Sources	All Methods						1.00	1.8	0.7	1.2

(*) These streams include listed "F" and/or "K" RCRA wastes.

computed using fractional waste generation rates that excluded water and the overall results were very similar.

The current reduction index (CRI) is a measure of reduction of waste that would be generated if none of the methods listed were implemented to their current level of application. For the phenolic resin industry, CRI is 1.8 (45 percent) which is indicative of the significant level of waste minimization that already has taken place.

The future reduction index (FRI) is an indication of the level to which the currently generated waste can be reduced if all of the techniques noted were implemented according to their rated potential. The FRI value of 0.7 to 1.2 (18 to 30 percent) is indicative of the moderate extent of future waste reductions. Among the techniques that were found most effective and applicable (as evidenced by high FRI value) for control of wastes were the use of a two-step rinse with recycle, the use of a counter-current rinse, and recycling of waste phenol.

10. PRODUCT SUBSTITUTION ALTERNATIVES

In 1980, about 27 percent of the phenolic resins were used as a binder for making plywood. This demand depends on the extent of use of pine from the Pacific Northwest instead of southern pine. Southern pine, due to its higher absorbency, requires almost 20 percent more resin than northwest pine (SRI 1981). Phenolic resins are also used as binders for fibrous and granulated wood to make waferboards. Injection molded thermoplastics can be effectively used to make waferboards, thus avoiding the use of phenolic resins.

In 1980, about 7 percent of phenolic resins were used for making decorative and commercial laminates. Use of thinner boards for vertical use as opposed to thicker horizontal boards will lower the amount of phenolic resin per square foot of the decorative laminate. Low-pressure polyester and melamine laminates, which do not use phenolic resins, or epoxy or silicone resin substitutes are some other possibilities.

11. CONCLUSIONS

Since phenolic resin manufacturing produces a relatively high quantity of waste, waste reduction by source control deserves special attention. Our qualitative estimates indicate that the possible waste reductions range from 18 to 30 percent. Several methods that appear to be quite effective for the industry as a whole are the two-step rinse method with the recycle of the first rinse, recovery and recycle of phenol from aqueous wastes, segregating of wash water from the receiver contents, and reuse of wash water.

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13. INDUSTRY CONTACTS

M.J. Kowalski. Manager, Environmental Compliance, Reichhold Chemicals, Inc., White Plains, NY.

1. PROCESS: PRINTED CIRCUIT BOARD MANUFACTURE

2. SIC CODE: 3679 (052)

3. INDUSTRY DESCRIPTION

Manufacturers of printed circuit boards (PCB's) are included as part of the electronic component manufacturing industry.

3.1 Company Size Distribution

As of 1984, the PCB manufacturing industry included a total of 585 plants* with a total employment of 435,100 (NCO 1984). The industry consists of large facilities which are totally involved with PCB's, large and small captive facilities, small job shops doing contract work, and specialty shops doing low-volume and high-volume precision work. Approximately half of the PCB's produced are by independent producers, while the rest are by captive producers. Table 3-1 lists company size distribution in the U.S.

Table 3-1 Company Size Distribution

	Number of Employees per Facility							
	Total	1-50	51-100	101-500	501-1000	1001-2500	2501-5000	5000+
No. of establish-ments	585	177	109	151	42	49	14	43
No. of employees	435,100	4,425	8,175	37,750	31,500	85,750	52,500	215,000

Source: Electronic Marketing Directory (NCO 1985).

* Industry contacts indicate that the actual number may be closer to 1000 plants.

3.2 Principal Producers

The ten major PCB producers in the U.S. are listed below (PEI 1983):

TRW Cinch Graphite	Western Electric
Texas Instruments	Rockwell International
Motorola Semiconductor	Syn-thane-Taylor
Microtran	Cincinnati Millacron
GTE Sylvania	Chicago Etching

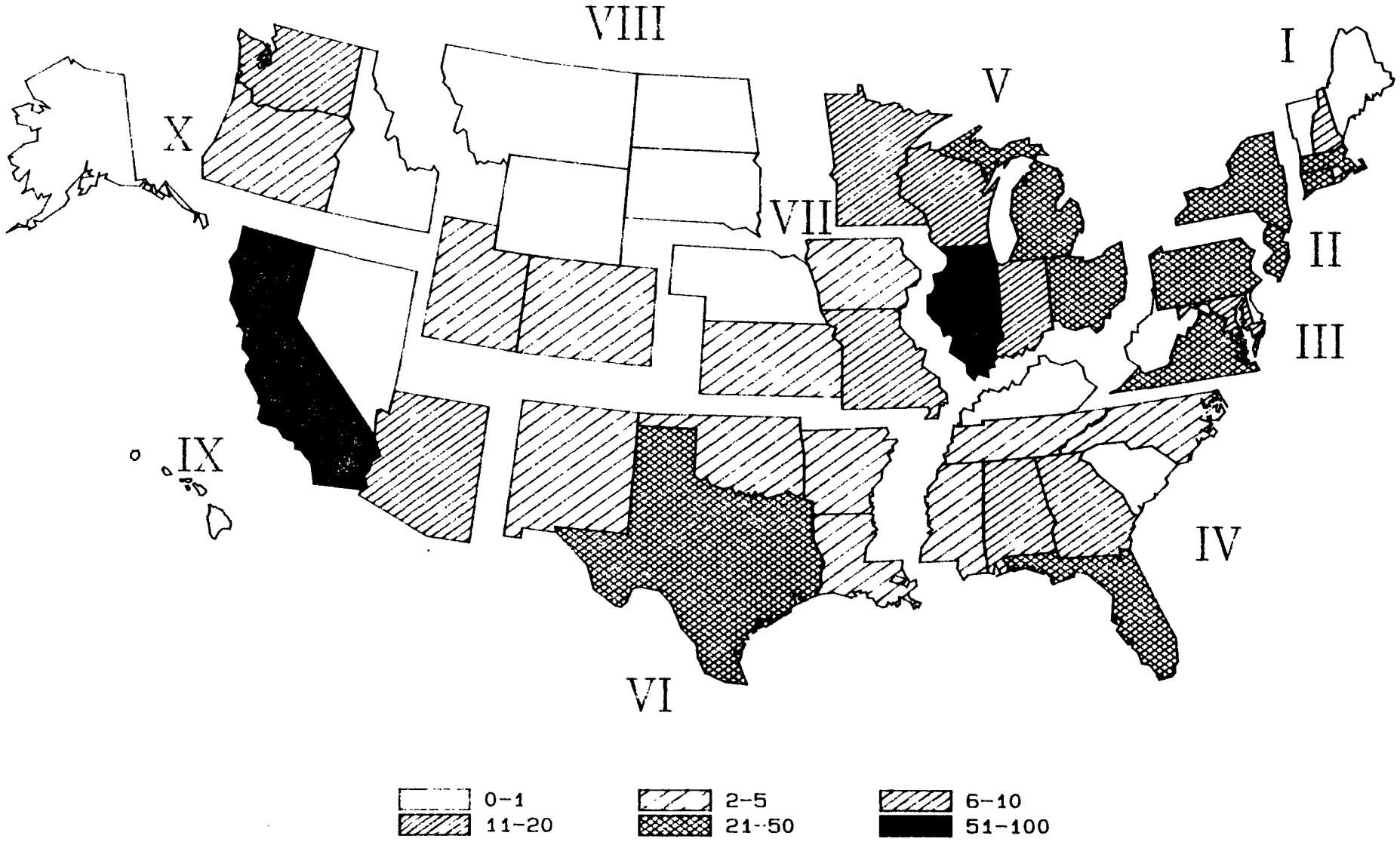
3.3 Geographical Distribution

Over 65% of all PCB manufacturing sites are located in the northeastern states and in California. The remaining plants are scattered throughout the country as represented by Figure 3-1 and Table 3-2 below.

Table 3-2 Geographical Distribution of Printed Circuit Board Manufacturing Facilities by EPA Region

EPA Region	Number of Employees per Facility							
	1-50	51-100	101-500	501-1000	1001-2500	2501-5000	5001+	Total
I	16	12	23	3	7	4	4	69
II	39	14	19	7	8	1	3	91
III	12	8	12	3	4	0	2	41
IV	18	13	11	5	4	3	2	56
V	42	37	43	10	12	2	15	161
VI	11	4	10	2	2	1	4	34
VII	2	1	5	1	2	0	4	15
VIII	1	1	2	1	0	1	0	6
IX	33	18	23	9	8	2	8	101
X	3	1	3	1	2	0	1	11
National	177	109	151	42	49	14	43	585

Source: Electronic Marketing Directory (NCO 1985).



B11-3

Roman numerals show EPA regions

Figure 3-1 Printed Circuit Board Plants in the U.S.

4. PRODUCTS AND THEIR USE

PCB's can be classified into 3 basic types: single-sided, double-sided, and multilayered. The total board production in 1983 was estimated at 14 million square meters (PEI 1983). Double-sided boards accounted for about 55 percent of the PCB's produced, while the percentage of multi-layer board production was 26 percent (PEI 1983). The type of board produced depends on the spatial and density requirement, and on the complexity of the circuitry. PCB's are used mainly in the production of business machines, computers, communication equipment, and home entertainment equipment.

5. RAW MATERIALS

The following raw materials are used by the industry (Stintson 1983, PEI 1983, Cox and Mills 1985):

Board materials	glass-epoxy, ceramics, plastic, phenolic paper, copper foil
Cleaners	sulfuric acid, fluoroacetic acid, hydrofluoric acid, sodium hydroxide, potassium hydroxide, trichloroethylene, 1,1,1-trichloroethane, perchloroethylene, methylene chloride
Etchants	sulfuric and chromic acid, ammonium persulfate, hydrogen peroxide, cupric chloride, ferric chloride, alkaline ammonia
Catalysts	stannous tin, palladium chloride
Electroless copper bath	copper sulfate, sodium carbonate, sodium gluconate, Rochelle salt, Versene-T, sodium hydroxide, formaldehyde
Screen	silk, polyester, stainless steel
Screen ink	composed of oil, cellulose, asphalt, vinyl or other resins
Resists	polyvinyl cinnamate, allyl ester, resins, isoprenoid resins, methacrylate derivatives, poly-olefin sulfones

Sensitizers	thiazoline compounds, azido compounds, nitro compounds, nitro aniline derivatives, anthones, quinones, diphenyls, azides, xanthone, benzil
Resist solvents	xylenes, toluene, benzene, chlorobenzene, cellosolve and cellosolve acetate, butyl acetate, 1,1,1-trichoroethane, acetone, methyl ethyl ketone, methyl isobutyl ketone.
Electroplating baths	copper pyrophosphate solution, acid-copper sulfate solution, acid-copper fluoroborate solution, tin-lead, gold, and nickel plating solutions
Resist stripping solutions	sulfuric-dichromate, ammoniacal hydrogen perioxide, metachloroperbenzoic acid, methylene chloride, methyl alcohol, furfural, phenol, ketones, chlorinated hydrocarbons, non-chlorinated organic solvents, sodium hydroxide

6. PROCESS DESCRIPTION

Three principal production methods have been employed by the industry to produce printed circuit boards. These include:

- -- The conventional subtractive process
- -- The fully additive process
- -- The semi-additive process

Detailed descriptions of the process sequences are given elsewhere (Yapoujian 1982, Coombs 1979, USEPA 1979, PEI 1983). Because of the limitations of the additive processes, the subtractive method is currently the most widely used method. Figure 6-1 illustrates the procedure for the production of double-sided panels using the subtractive method (Yapoujian 1982). Most of the operations shown are also common to the production of other types of printed circuit boards such as single-sided or multi-layered boards.

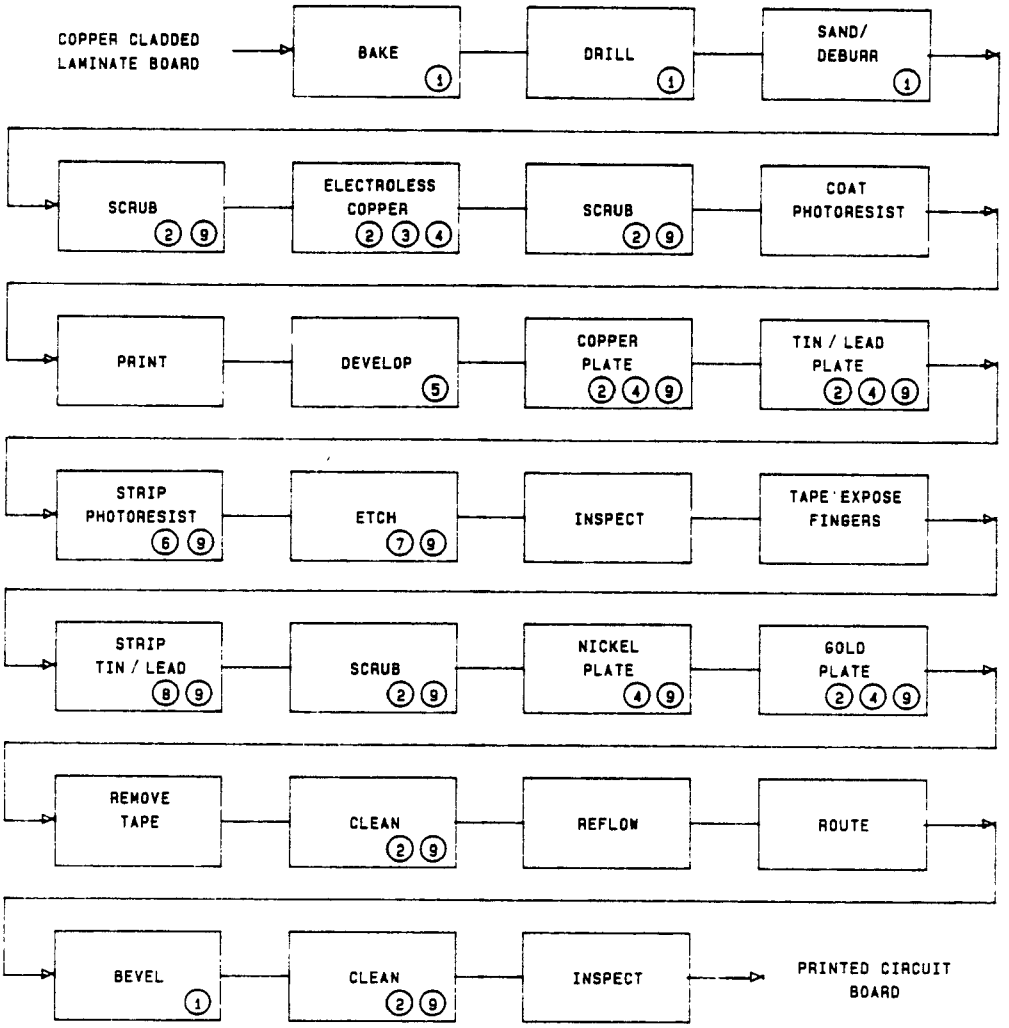


Figure 6-1 Substractive Process for the Production of Double-sided Printed Circuit Boards

The conventional subtractive process starts with a copper-cladded laminate board, composed of a non-conductive material such as glass epoxy or plastic. PCB manufacturers often purchase panels of board that are already copper cladded from independent laminators to use as the starting material for the PCB's. The manufacturing process consists of the following operations:

Board preparation - The process sequence begins with a baking step to ensure that the copper laminated boards are completely cured. Holes for the components are then drilled through stacks of boards or panels, often 4 layers thick. The drilling operation results in burrs being formed on one or both sides of the panel. These are removed mechanically through sanding and deburring steps to create an even surface.

Electroless copper plating - The smooth copper-cladded board is subsequently electroless plated with copper to provide a conducting layer through the drilled holes for circuit connections between the copper-cladded board surfaces. Electroless plating involves the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent. The metal is therefore deposited without the use of external electrical energy. The circuit board must be thoroughly cleaned before it is electroless plated. The typical steps for electroless plating are:

-- Mechanically scrub and alkaline clean the boards to remove soil and fingerprints. This is followed by a rinsing step usually involving spray or counter flow rinsing with water.

-- Etch the copper-cladded surface. The board is immersed in ammonium persulfate or a peroxide-sulfuric acid mixture to remove the oxidation inhibitor in the copper foil. This provides for better adhesion of the electroless plating catalyst. After etching, the board is again rinsed.

-- Catalyst application. This step is required for through-hole plating. A catalyst must be applied for the initial metal deposition to occur on non-metal surfaces, such as the interiors of the holes. Catalysis is done by a stabilized reaction product of stannous chloride and palladium chloride which is often sold as concentrated solution in hydrochloric acid. The resulting board will consist of a surface layer of palladium nuclei, and

stannous and stannic hydrous oxides and oxychlorides. Following catalyst application, the board is rinsed with water.

-- Surface activation. The catalyzed board is immersed in a solution that dissolves away the excess tin, exposing the molecular layer of palladium metal on the board surface. The palladium then acts as the base for electroless copper deposition. Following surface activation, the board is rinsed.

-- Electroless plating. The board is immersed in an electroless copper plating bath. The plating bath usually consists of a copper salt such as cupric chloride or copper sulfate. The reducing agents most often used to reduce the metal to its base state are formaldehyde and hypophosphate. In addition, chelating agents are also added to the plating bath to hold the metal in solution, preventing plate-out on the tank wall. The four most common types of chelating agents used are amino acids, carboxylic acids, hydroxy acids, or amines. Following plating, the board is rinsed and mechanically scrubbed.

Pattern printing and masking - After the board is electroless-plated with copper to provide a uniform conducting layer over the entire surface, the board can be panel plated or pattern plated to produce the desired circuitry. Panel plating consists of copper electroplating the entire board area, including holes, immediately following the electroless copper plating. A metal etching resist is then plated onto the copper board in a pre-determined pattern. The board is subsequently etched to provide the desired circuitry. Pattern plating, on the other hand, consists of copper electroplating only the holes and circuitry. Since pattern plating is more commonly used in the industry, the steps involved in this operation are described below.

In pattern plating, a plating resist is applied to produce the circuit image on the board. The resist is a resin whose function is to provide a protecting layer over areas of a substrate that are not to be affected by a subsequent etching or plating process. There are two main ways in which a resist can be applied onto the board. These are screen-printing and photolithography.

In the screen-printing method, ink is forced through unblocked spaces in a stainless steel mesh or synthetic fabric screen and onto the board. The ink is then cured by heating or by exposing the board to UV light, and thus produces the desired image of the circuit pattern on the board.

The second method relies on exposing a light-sensitive resist to light through a patterned glass or a photographic film master called a phototool (or photo mask). There are many types of photoresist on the market. These include liquid or dry film, which can be either negative or positive resists. A negative resist is a resin whose solubility in the developer is greater for the areas which are unexposed to light. This will lead to the formation of a pattern by the removal of unexposed zones when the board is dipped into a developing solution. The common types of negative resist used are epoxy, vinyl polymers, or halogenated aromatics.

A positive resist is more soluble in the developing solution in the light-exposed areas. Therefore, a pattern will be formed by the removal of the exposed areas. The different types of positive resist are: methacrylates, halogenated methacrylates, cross-linked methacrylates, or polyolefin sulfones.

To transfer a circuit image onto the board, the board must be coated either with a liquid resist or a dry film resist. Liquid resist can be applied to the panel by immersing it into the solution and withdrawing it at a controlled rate. The coated board is then dried, and the pattern is printed onto the board by exposing it to UV light through a photo mask. Dry film resist is a photo-sensitive resin, sandwiched between a polyethylene and a polyester layer. To apply the dry film resist, a polyethylene layer is peeled off and the bare resin surface is laminated onto the board. The printing of the circuit image can then be done by exposing the board to UV light with a photo mask. The remaining polyester film is then peeled off before developing.

After the photoresist-coated surface has been printed by exposure to UV light, the desired circuit pattern can be produced through a developing process. The developer can be an organic solvent, or an alkaline aqueous-based solution, depending on the type of resist being used. The developing solution will dissolve away the resist in unwanted areas, leaving behind a pattern of copper-exposed areas for subsequent plating. This operation is usually done by immersing the panels in a still developer solution, a spray tank, or a conveyorized system.

Electroplating - After a pattern is developed onto the board, the circuit is built up through a copper electroplating process. The steps involved in the copper electroplating operation include:

-- Alkaline clean to remove any residual from the developing operation and then rinse.

-- Light etch to ensure the removal of any residual photoresist not already removed in the developing of the image. The board is usually immersed in a light etching solution, such as peroxide-sulfuric acid or sodium persulfate. Following this step, the board is rinsed.

-- Acid dip to remove oxides and then rinse.

-- Copper electroplating. The boards are immersed in a copper plating bath. The bath contains copper salts dissolved in alkaline cyanide, acid sulfate, pyrophosphate, or fluroborate solutions. The pattern or circuitry is thus built up to the desired thickness. This step is then followed by rinsing.

After the circuit is copper electroplated, tin/lead is used as a resist for the subsequent etching process. The procedure for tin/lead electroplating is similar to the copper electroplating process described previously. However, the tin/lead electrolyte is very sensitive to contamination by sulfates. Therefore, care must be taken to prevent drag-in from the pre-cleaning operations. After the board is tin/lead plated, the original plating resist is stripped off by immersing the boards in resist stripping solutions such as caustic, methylene chloride, glycol ethers with caustic, or glycol ethers with amines/ammonia. The boards are then thoroughly rinsed with water.

Etching - The removal of the original plating resist results in exposed areas of unwanted copper. In batch etching, which is rarely used now, the panels are immersed in a still tank containing an etching solution until all the unwanted copper is etched away. In etching using a conveyorized system, panels are placed on a conveyor, and etchant is sprayed on them. The most common types of etchant are: ferric chloride, cupric chloride, chromic acid, ammonium persulfate, peroxide-sulfuric acid, and ammoniacal etchants. Chromic acid used to etch tin/lead plated panels has been virtually eliminated due to effluent guidelines; however, it is still used to etch epoxy smears following the drilling of multilayer boards.

Copper etching represents the last major operation involved in the manufacturing of printed circuit boards. The boards are subsequently cleaned and electroplated with different types of metals, such as nickel and gold, to provide solderability and corrosion protection. The procedures for these operations, however, are similar to the one described previously for copper electroplating.

The fully additive method differs from the subtractive method described above in that it involves the deposition of the plating material onto the board in the pattern dictated by the circuit, as opposed to the removal of the metal already deposited through etching. The process begins with an uncladded board. Plating resist is then applied onto the board in non-circuit areas. Electroless copper is subsequently deposited to build up the circuit to the desired thickness. Since the board doesn't initially have any copper in non-circuit areas, a copper etching step is thus eliminated.

7. WASTE DESCRIPTION

There are 5 principal operations common to the production of all types of printed circuit boards. These include:

- -- Cleaning and surface preparation
- -- Catalyst application and electroless plating
- -- Pattern printing and masking
- -- Electroplating
- -- Etching

Typical waste streams generated from the unit operations in the printed circuit board manufacturing industry are listed in Table 7-1.

Airborne particulates generated from the cutting, sanding, routing, drilling, beveling, and slotting operations during board preparations are normally collected and separated using bag-house and cyclone separators. They are then disposed of, along with other solid wastes, at landfills.

Acid fumes from acid cleaning and organic vapors from vapor degreasing are usually not contaminated with other materials, and therefore are often kept separate for subsequent treatment. The acid fume air stream is collected via chemical fume hoods,

Table 7-1 Waste Streams from Printed Circuit Board Manufacturing

Waste Source	Waste Stream Description	Waste Stream Composition	RCRA Code
Cleaning/Surface preparation	1. Airborne particulates 2. Acid fumes/organic vapors 3. Spent acid/alkaline solution 4. Spent halogenated solvents 5. Waste rinse water	board materials, sanding materials, metals, fluoride, acids, halogenated solvents, alkali	F001, F002
Catalyst application/ Electroless plating	1. Spent electroless copper bath 2. Spent catalyst solution 3. Spent acid solution 4. Waste rinse water	acids, stannic oxide, palladium, complexed metals, chelating agents.	--
Pattern printing/masking	1. Acid fumes/organic vapors 2. vinyl polymers, 3. Spent resist removal solution 4. Spent acid solution 5. Waste rinse water	F003, F005 chlorinated hydrocarbons, organic solvents, alkali	
Electroplating	1. Spent plating bath 2. Waste rinse water	Copper, nickel, tin, tin/lead, gold, fluoride, cyanide, sulfate.	F006, F007, F008, F009
Etching	1. Spent etchant 2. Waste rinse water	ammonia, chromium, copper, iron, acids.	--

and sent to a scrubber where it is contacted with water. The scrubbed air then passes on to the atmosphere, and the spent absorbing solution is treated along with other acidic waste streams. Similarly, organic fumes are often collected and passed through a bed of activated carbon. The carbon bed is then regenerated with steam. In many cases, the regenerative vapor is condensed and the condensate containing water and solvents is drummed and land disposed. In a few cases, the regenerative vapor is combusted.

The spent acid and alkaline solutions from the cleaning steps are either contract hauled for offsite disposal or pH-treated to precipitate out the contaminants. The precipitates are removed by clarification, filtration, or flotation, and the resulting sludge is hauled away for disposal or recovery. Spent chlorinated organic solvents are often gravity separated, and are recovered in-house or hauled away for reclaiming.

The remaining majority of the wastes produced are liquid waste streams containing suspended solids, metals, fluoride, phosphorus, cyanide, and chelating agents. Low pH values are often the characteristic of the wastes due to acid cleaning operations. The liquid wastes may be controlled using end-of-pipe treatment systems, or a combination of in-line treatment and separate treatment of segregated waste streams. A traditional treatment system for the wastes generated is often based on pH adjustment, or on the addition of chemicals that will react with the soluble pollutants to precipitate out the dissolved contaminants in a form such as metal hydroxide or sulfate. The solids are removed as a wet sludge by filtration or flotation, and the water is discharged to the sewer. The diluted sludge is usually thickened before dumping into landfills. Recent improvements in in-line treatment technologies such as reverse osmosis, ion exchange, membrane filtration, and advanced rinsing techniques increase the possibility for the recovery and reuse of water and metals.

8. WASTE GENERATION RATES

Very little data was available on specific waste generation rates from the printed circuit board manufacturing industry. Typical concentration values of principal pollutants present in wastewater were reported previously (USEPA 1979). Principal pollutants included suspended solids, cyanide, copper, nickel, lead, chromium, fluoride, phosphorus, and several noble metals. While no specific waste generation rates were

reported, fractional rates were estimated by project staff based on the available information and engineering judgement. These values are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

A summary of the waste sources and the corresponding source reduction methods is given in Table 9-1. This section deals with the description of the listed techniques.

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" has also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel practices
  - -- management initiatives
  - -- employee training
- o Procedural measures
  - -- documentation
  - -- material handling and storage
  - -- material tracking and inventory control
  - -- scheduling
- o Loss prevention practices
  - -- spill prevention
  - -- preventive maintenance
  - -- emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Cleaning and Surface Preparation

The majority of the waste generated by this operation comes from various rinsing steps. Since a substantial amount of water is often required, treatment of contaminated rinse water presents a major problem in waste disposal for the printed circuit board manufacturing industry. The rinse water is often pH treated, and the resulting sludge hauled away for disposal or recovery. The less contaminated water is then discharged.

Source reduction methods for the minimization of wastes generated from different cleaning operations have been described in a separate study of metal parts cleaning practice included in this appendix. Since a very high water usage rate is a major characteristics of the printed circuit board manufacturing industry, reduction of the amount of water used will greatly improve the waste treatment process along with reducing the precipitated calcium and magnesium salts which are present in the treatment sludges together with heavy metal precipitates. The reader is referred to the study mentioned above for appropriate source reduction methods for the cleaning and surface preparation operations in the manufacturing of PCB's.

9.1.2 Catalyst Application and Electroless Plating

The waste streams generated from this operation are liquids which are either spent process solutions or waste rinse water. Generally, pH adjustment and clarification are used to precipitate out the contaminants. The source reduction techniques include:

- Use combined sensitization and activation solution to eliminate one extra rinsing step.

  Some PCB manufacturers are using this technique in the manufacturing process. Others prefer to use separate application and activation steps since it seems to improve the activity of the catalyst. The reduction of waste resulting from the elimination of one extra rinsing step, however, should outweigh the disadvantage of reduced catalyst activity. The opinions on the technical merit of this technique appear to be split.

- Use lower concentration plating bath to reduce the degree of subsequent rinsing required.

This approach has been tried mostly by large companies in the electroplating industry. No available information has been reported from PCB manufacturers on the use of plating baths with lower concentrations.

- Use differential plating instead of the conventional electroless plating process.
  By controlling the concentration of certain stabilizers in the electroless copper bath, copper will be deposited three to five times faster on the through-hole walls than on the copper cladded surface (Poskanzer and Davis 1982). This process will reduce the amount of copper which must be subsequently etched away in the subtractive method. The use of differential electroless plating has not been reported by PCB manufacturers and it may require significant developmental work before commercialization is possible.

- Use weak or biodegradable chelating agents.
  The use of weak agents will allow more effective metal removal in subsequent metal recovery operations, and thus reduce the amount of waste discharged. Only a small number of PCB manufacturers have reportedly been using weak chelating agents such as hydroxy acids in the electroless plating bath.

- Use in-line techniques for metal recovery.
  Metal recovery units, such as an ion-exchange columns, should be installed in-line to remove metals from spent plating baths and waste rinse waters. The ion-exchange resin can be periodically regenerated to provide plating solutions which can then be recycled to the plating bath. Large PCB manufacturing plants have begun to install metal recovery units on-site to recover metals from wastewaters. However, since these units are generally used to remove different metals from a combined waste stream, regeneration of the plating bath solution is not being practiced.

- Use computerized/automated control systems.
  Computerized process-control systems can be used for board handling and process bath monitoring to prevent unexpected decomposition of the plating bath. Since the use of a computerized control system not only

requires a large capital outlay for initial installation but also increases the demand for skilled operations and maintenance personnel, only very large companies which manufacture both PCB's and other electronic components are incorporating this change in their manufacturing process. For example, Hewlett-Packard in Sunnyvale, California reported its successful use of computers for plating operations on PCB's (Anonymous 1983). The majority of PCB manufacturing plants, however, are small and therefore can only utilize automated handling of the boards in the plating operations.

- Better operating practices.

  Due to their simplicity and low cost, good operating practices are widely used in the industry as the first effort to reduce the waste generated. Some of the methods used are frequent inspection of plating racks for loose insulation to prevent excessive dragout of process solution, distributing the work load evenly to avoid dense loading which can cause localized instability of the process solution, and stripping copper out of the plating tank regularly to prevent continuous deposition of copper and palladium on the tank walls.

  Another approach is to segregate all waste streams. Chelated waste streams should be separated from other streams to prevent problems in precipitating out the metals during subsequent waste treatment. Segregation of complexed copper streams is widely practiced in the industry to reduce the volume of waste generated.

9.1.3 Pattern Printing and Masking

Depending on the chemicals used, air emissions consist of various organic compounds. The fumes are usually collected and passed through an activated carbon bed. The remaining liquid waste streams are spent chlorinated solvents, spent resist solution, and waste rinse water. The organic solvents and resists are gravity separated and collected for disposal or recovery. The following source reduction techniques were noted:

- Use aqueous processable resist instead of solvent processable resist.
  Aqueous processable resists, such as the Du Pont Riston photopolymer film resists which allow for the use of caustic and carbonates as developer and stripper*, can be used in place of solvent processable resists whenever possible to eliminate the generation of toxic spent solvents. Hundreds of facilities are now using these aqueous processable films for the manufacturing of PCB's.

- Use screen-printing instead of photolithography to eliminate the need for developers.
  Screen-printing has conventionally been used only to produce PCB's which require very low resolution in the width and spacing of the circuit lines. Some companies have recently developed screen-printing techniques which can provide higher degrees of resolution. For example, General Electric has developed a method for screen-printing down to 0.01 inch resolution which can be used to manufacture PCB's for appliances (Greene 1985). The majority of PCB manufacturers, however, are still using the photolithographic technique for PCB's having circuitry finer than 12 mil lines and spaces.

- Use Asher dry photoresist removal method to eliminate the use of organic resist stripping solutions.
  Although this method is increasingly being used in the semiconductor industry, its use has not been reported by PCB manufacturers, probably because the PCB resists are usually much thicker than the corresponding semi-conductor resist layers. Additional exploration is suggested.

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* E.I. Du Pont de Nemours & Co. 1985: Personal communication.

9.1.4 Electroplating

Electroplating waste streams consist mainly of rinse water and contaminated or spent dumps of plating solutions. The dissolved metals are often precipitated out by pH adjustment, and are contract hauled for metal recovery or disposal. Cyanide-containing waste must be oxidized using chlorine or other strong oxidants. The source reduction techniques which are used to minimize the wastes generated from the electroplating operation are given in a separate process study on electroplating (B3). The source reduction method considered specific to the manufacturing of PCB's is the use of pattern plating instead of panel plating:

- Use pattern instead of panel plating.
  Since panel plating consists of copper plating the entire board area, while pattern plating requires copper electroplating only the holes and circuitry, the use of the latter technique will reduce the amount of non-circuit copper which must be subsequently etched away. This practice can therefore reduce the amount of waste generated from the etching operation. The switch from panel to pattern plating has been made by a large number of PCB manufacturers. Customers demanding applications for a uniform cross section of circuitry in computer and microwave PCB's, however, may dictate the use of panel plating to provide highly uniform copper thickness.

9.1.5 Etching

Spent etchant and rinse water are the main waste streams generated from this operation. As with electroplating, the metals are precipitated out of the waste stream by pH adjustment. The following source reduction techniques were noted:

- Use dry plasma etching techniques.
  The need for toxic etching solutions can be eliminated by using a dry etching technique (Till and Luxon 1982). Etching can be done either chemically using reactive gaseous radicals, or physically using non-reactive ion bombardment. Radio-frequency sources can be used to ionize gaseous molecules to create plasma. The etching products can then be removed by vacuum pumps. The use of dry etching techniques has not been reported by

PCB manufacturers. A separate study can to examine the applicability of this technique in removing thick copper layers (1.4 mil) which are used in PCB manufacture.

- Use additive instead of subtractive method.
  This change will eliminate the copper etching step, and therefore eliminate the generation of substantial volumes of spent etchant as well as reduce the amount of metal hydroxide sludges generated. Although subtractive is still the most widely used method in the manufacturing of PCB's, the additive method is gaining in popularity since its use results in less waste and lower manufacturing costs (Brush 1983). A noted drawback to the additive method, however, lies in the fact that additive processing requires the use of solvent processable instead of aqueous processable photo-resists*. Futhermore, spent additive plating bath often contains heavily complexed copper which may result in waste treatment problems.

- Use less toxic etchant.
  Non-chromium etching solution has reportedly been used by PCB manufacturers in an effort to reduce the toxicity of the waste generated.

- Use in-line techniques for metal recovery.
  Bend Research, Inc., has recently developed a metal recovery technique using liquid membranes, which can be used to remove copper from PCB etching solution (Basta 1983).

- Use thinner copper foil to clad the laminated board.
  This change will reduce the amount of copper which must be etched, and thus will reduce the amount of waste generated from the etching process. PCB manufacturers are switching to boards cladded with thinner copper as their starting materials.

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* E.I. Du Pont de Nemours & Co. 1985: Personal communication.

9.2 Implementation Profile

The amount of hazardous waste generated by the printed circuit board industry has been and can be further reduced through implementation of the source reduction techniques outlined above. Many of these techniques are currently practiced, which demonstrates their technical and economic feasibility.

Basic improvements in operating practices can yield substantial savings in raw material disposal and treatment costs at little expense to the manufacturer. For example, frequent rack equipment inspection for loose insulation can prolong the integrity of process solutions, thereby reducing the rate at which the solutions are replaced. Segregating chelating agents from solutions containing metals enhances the feasibility of recovery of these metals from the solutions. Improvements in the process itself may require significant outlays of capital and increases in operating cost. The economic feasibility of such proposed improvements should be examined carefully and should include proper consideration of avoided costs.

Specific to the PCB manufacturing industry, implementation of major source reduction techniques such as the use of the additive instead of the subtractive method, or the substitution of materials and/or techniques associated with the electroless plating and electroplating processes, might be promoted effectively through guidelines, technical assistance, and information programs. A majority of the PCB manufacturers are small companies who may have difficulties in conducting extensive research and testing to assure the performance of modifications in the manufacturing process.

9.3 Summary

The summary of all noted source control techniques is given in Table 9-1. Each technique was rated for its effectiveness, extent of current use and future application potential on scale of 0 to 4. The ratings were derived by project staff based on review of the available data and in consultation with the industry. The estimates of current level of waste reduction achieved (current reduction index) and possible future reduction (future reduction index) were obtained from the ratings in accordance with the methodology presented in the introduction to this appendix.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE PRINTED CIRCUIT BOARD MANUFACTURING INDUSTRY

Waste Origin	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Cleaning/Surface Preparation (*)	1. See study on Metal Parts Cleaning	---	---	---	---	---		2 0	1.2	1 9
	Overall	---	---	---	---	---	0 15	2.0	1.2	1 9
Catalyst Activation and Electroless Plating	1. Use combined sensitization/activation	2	1	2	2	2		1.0	0.5	
	2. Use lower concentration plating bath	1	1	2	1	2		0.5	0.8	
	3. Use differential electroless plating	0	0	3	0	3		0.0	2.3	2.3
	4. Use weak/biodegrade chelating agents	1	1	2	2	2		1.0	0.5	
	5 Use in-line metal recovery techniques	3	3	3	2	2		1.5	0 6	
	6. Use computerized/automated control	1	1	2	2	3		1 0	0.8	
	7. Better operating practices	3	3	3	2	2		1.5	0.8	
	Overall	1 57	1 43	2 43	1.57	2 29	0.21	1 5	0.9	2 3
Pattern Printing/ Masking (*)	1. Use aqueous processable resists	2	1	2	1	3		0.5	1.1	1 1
	2. Use screen print instead of photolith	1	1	2	3	1		1.5	0.1	
	3. Use Asher dry resist removal method	1	1	1	0	1		0.0	0.3	
	Overall	1.33	1.00	1.67	1 33	1.67	0 05	1.5	0.5	1.1
Electroplating (*)	1 See study on Electroplating	---	---	---	---	---		1.8	0.8	1 9
	2. Use pattern instead of panel plating	1	1	3	3	1		2.3	0.2	
	Overall	---	---	---	---	---	0 44	2.3	0.5	1.9
Etching	1. Use dry plasma etching techniques	0	0	3	0	2		0 0	1.5	1 5
	2 Use additive in place of sub method	2	2	3	1	1		0.8	0.6	
	3. Use less toxic etchants	1	1	2	2	2		1 0	0.5	
	4. Use in-line metal recovery techniques	3	3	3	2	2		1.5	0.8	
	5. Use thinner copper foil for cladding	1	1	2	2	1		1.0	0.3	
	Overall	1 40	1.40	2 60	1 40	1 60	0.15	1.5	0.7	1.5
All Sources	All Methods						1 00	2.0	0.7	1 9

(*) These streams include listed "F" and/or "K" RCRA wastes

Based on these ratings, it is estimated that the currently achieved level of waste minimization is significant, as evidenced by the current reduction index (CRI) of 2.0 (50 percent). CRI is a measure of reduction of the potential waste that would have been generated, if none of the techniques listed in Table 9-1 were used at their present levels.

By additional implementation of the techniques listed, it is estimated that the extent of future waste reductions can be characterized as moderate to significant, as evidenced by the future reduction index (FRI) of 0.7 to 1.9 (18 to 48 percent).

The techniques that offer most promise to contribute significantly to waste reduction in the future are the ones characterized by a high FRI. It appears that the use of more efficient cleaning techniques (see study on metal parts cleaning), along with differential electroless plating, use of aqueous processable resist, source control in electroplating operation (see study on electroplating), and use of dry plasma etching are the most promising for the entire industry. However, each installation is unique and will evaluate only those options that have the highest application potential for their specific needs.

10. PRODUCT SUBSTITUTION ALTERNATIVES

Improvements in the techniques used in the packaging of microchips can alter the design of PCB's significantly and result in a decrease of waste associated with PCB manufacturing. Presently, the dual-in-line package (DIP) accounts for 80% of all packaging of integrated circuits (Bowlby 1985). More efficient packages, however, are being developed which utilize a relatively new method of attaching packages to PCB. One important method is called surface mounting. The use of surface mounting instead of the conventional through-hole insertion mounting allows for closer contact areas of chip leads, and therefore reduces the size of PCB's required for a given number of packages or DIPS. For a fixed number of packages, the PCB needs to be only 35% to 60% as large as a PCB designed for the old style package (Bowlby 1985). As the metal area on which cleaning, plating and photoresist operations are performed is decreased, the wastes associated with these operations will also undergo a decrease.

In addition, the development of high-temperature, high-performance thermoplastics has introduced the use of injection molding into the manufacturing of PCB's. In this

process, heated liquid polymer is injected under high pressure into precision molds. Since the molded substrates are unclad, semiadditive or fully additive plating is used to produce metalized conductor patterns. (Eugelmaier and Frisch 1982). Injection molding, coupled with a fast-rate electrodeposition (FRED) technique, such as that developed by Batelle (LWVM 1985), can therefore be used to manufacture complex three-dimensional PCB's with possible reduction in hazardous waste generation due to the elimination of spent toxic etchants.

11. CONCLUSIONS

Waste reduction in the printed circuit board manufacturing industry has already been accomplished to a significant extent through the implementation of the source control techniques listed in Table 9-1. Additional waste reduction in the 18 to 48 percent range, can be expected by wider adoption of such techniques as more efficient cleaning, differential electroless plating, use of aqueous processable resist, source control of the electroplating operation, and use of dry plasma etching. In the area of product substitution, the use of surface mounting technology and the use of injection molding coupled with fast-rate electrodeposition appear to offer high future potential for waste reduction.

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13. INDUSTRY CONTACTS

Dr. G.J. Hollod, Senior Environmental Engineer, E.I. Du Pont de Nemours & Company, Wilmington, DE.

W.G. Vaux, P.E., Chemical and Process Engineering, Westinghouse Electric Corporation, Pittsburgh, PA.

1. PROCESS: PRINTING OPERATIONS
2. SIC CODE: 27
3. INDUSTRY DESCRIPTION

As defined in the Standard Industrial Classification Manual (USDC 1972), Major Group 27 - the printing, publishing, and allied industries include "establishments engaged in printing by one or more of the common processes, such as letterpress, lithography, gravure, or screen; and those establishments which perform services for the printing trade, such as bookbinding, typesetting, engraving, photoengraving, and electrotyping. This major group also includes establishments engaged in publishing newspapers, books, and periodicals, regardless of whether or not they do their own printing". Of the seventeen SIC subgroups under major group 27, about fifteen would involve substantial printing operation activities.

The graphic arts industry, as SIC 27 is otherwise referred to in this report, is one of the biggest in the United States, ranking highly among the twenty major manufacturing groups included in the SIC system. This is evidenced by the statistics shown in Table 3-1.

Table 3-1 1982 Ranking of the Graphic Arts Industry

Rank	Criteria	Value, U.S. dollars
First	in number of establishments	53,500
Sixth	in number of employees	1.3 million
Seventh	in total dollar payroll	$ 22.7 billion
Eighth	in value added by manufacturing	$ 49.4 billion
Tenth	in value of shipments	$ 85.8 billion
Tenth	in dollars reinvested in capital expenditures	$ 3.2 billion
Eleventh	in average hourly earnings	$ 8.58 per hour

Source: Printing Industries of America 1985: Personal communication.

3.1 Company Size Distribution

Of the 53,356 printing facilities located in the U.S., 80 percent employ less than 20 people each. Overall, the Bureau of the Census (USDC 1985a, 1985b, 1985c) estimated that 1,291,000 people were employed by the printing industry in 1982. Table 3-2 lists company size distribution as a function of total number of employees at a given site.

Table 3-2 1982 Company Size Distribution

	No. of employees per facility				
	1-19	20-49	50-99	100+	Total
No. of establishments	42,485	6,145	2,525	2,201	53,356
No. of employees (x 1,000)	231	187	175	698	1,291

Source: 1982 Census of Manufactures (USDC 1985a, 1985b, 1985c).

3.2 Principal Producers

The printing industry is composed of a small number of multi-plant firms and a large number of single plant firms. The six largest firms, in terms of sales and number of employees, are listed in Table 3-3 below.

Table 3-3 Principal Producers in the Graphic Arts Industry

Company	Sales (1984)	No. of Plants	Number of Employees
R.R. Donnelley & Sons (Chicago, IL)	$1.8 billion	17	17,700
Hallmark Cards (Kansas City, MO)	$1.5 billion	1	20,100
Moore Business Forms (Glenview, IL)	$1.4 billion	38	15,000
American Greetings (Cleveland, Ohio)	$945 million	7	23,000
Deluxe Check Printers (St. Paul, Minnesota)	$682 million	61	10,900

Source: American Printer (Anonymous 1985).

3.3 Geographical Distribution

Graphic arts establishments are scattered all over the United States, with the largest concentrations in California and New York. These two states share about 12 and 11 percent of the industry, respectively. Illinois, Texas, Florida, New Jersey, Pennsylvania, and Ohio each share about 5 percent of the total. Distributions by EPA region are shown in Table 3-4 and Figure 3-1. About 20 percent of the firms are located in Region V, and about 15 percent in Regions II and IX.

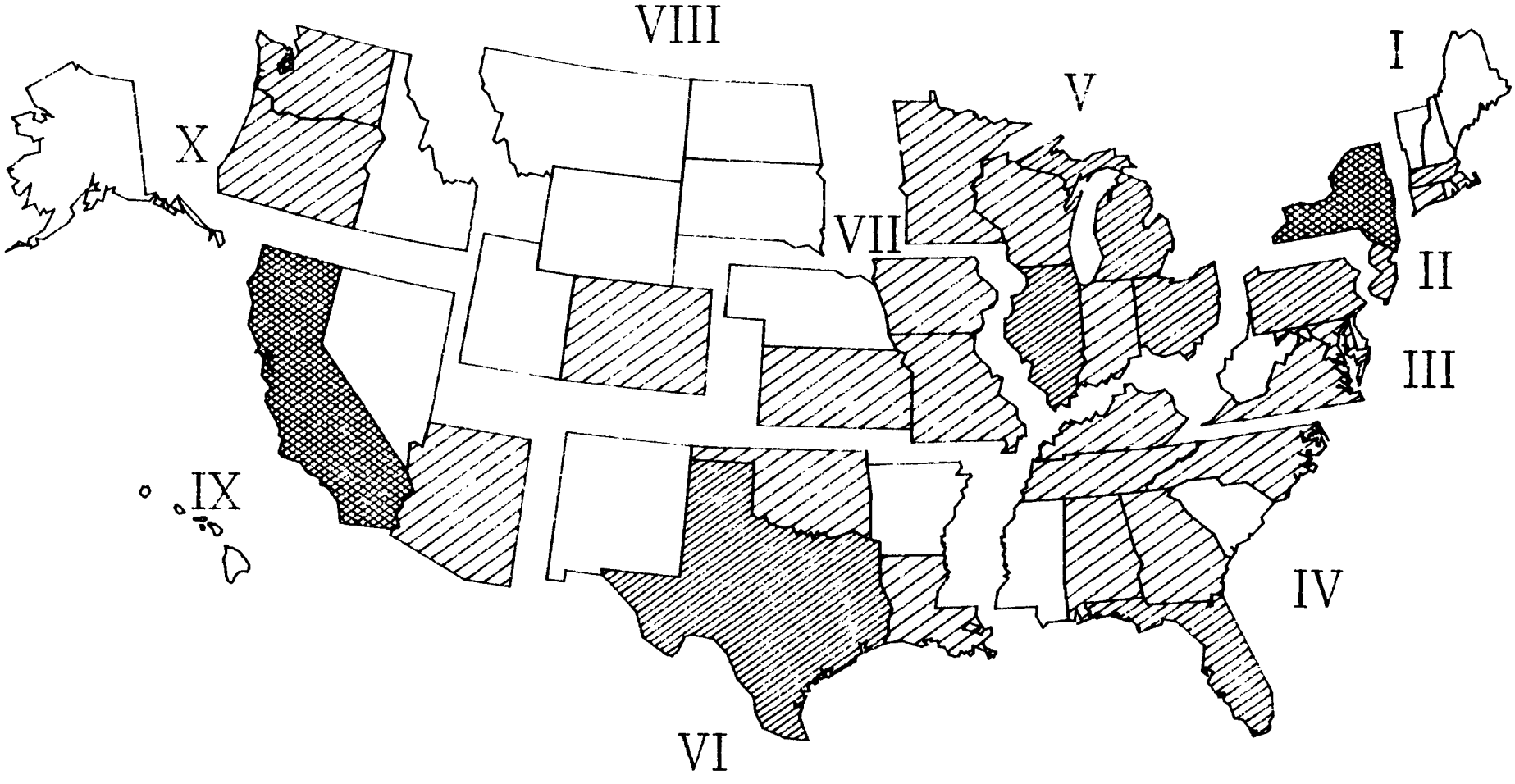
Table 3-4 Location of Facilities by EPA Region

EPA Region	Total No. of Facilities	Number of employees per facility	
		1-19	20+
I	3,458	2,625	833
II	8,203	6,420	1,783
III	4,359	3,203	1,156
IV	7,305	6,097	1,208
V	10,586	8,174	2,412
VI	4,985	4,111	874
VII	3,153	2,485	668
VIII	1,827	1,514	313
IX	7,530	6,237	1,293
X	1,800	1,519	281

Source: 1982 Census of Manufactures (USDC 1985d).

4. PRODUCTS AND THEIR USES

The graphic arts industry produces a large number of products such as newspapers, paper packaging containers, business forms, books, posters etc. (printed matter), and printing plates which serve various needs. These products fall under any one of the seventeen SIC subgroups. Table 4-1 lists the major sub-industries and the value of product shipments.



B12-4

Roman numerals show EPA regions

Figure 3-1 Printing Establishments in the U.S.

Table 4-1 Graphic Arts Industry: Value of Shipments in 1984

SIC	Industry	Value of Shipments[a] (in millions of dollars)
27	Printing and allied products	40,256
2711	Newspaper publishing and printing	9,890
2721	Periodical publishing and printing	5,932
2732	Book printing	3,585
2741	Miscellaneous publishing and printing	2,310
275	Commercial printing	11,600
2761	Manifold business forms	2,318
2771	Greeting card publishing and printing	1,228
2795	Lithographic platemaking services	830
-	Other printing and publishing	2,308

Source: 1984 U.S. Industrial Outlook (USDC 1984).

[a]Forecast estimate.

5. RAW MATERIALS

The principal raw materials used by the graphic arts industry are inks and substrates. A substrate is any material upon which ink is impressed, such as paper, plastic, wood, or metal. Table 5-1 shows the recent usage of ink and paper by the industry.

Table 5-1 Paper and Printing Ink used by the Graphic Arts Industry

Material	Volume (short tons)
Paper[a]	
Commercial printer	5,300,000
Magazines and other periodicals (other periodicals include catalogs and directories	4,000,000
Book	900,000
Printing Ink[b]	
Lithographic and offset	190,150
Gravure	179,750
Letterpress	119,250
Flexographic	91,150

Source: 1984 U.S. Industrial Outlook (USDC 1984); American Paper Institute 1985: Personal communication.
(a) Data are for 1984.
(b) Data are for 1982.

6. PROCESS DESCRIPTION

In the graphic arts industry, there are three major printing processes (offset lithography, gravure, and flexography). Two additional methods, letterspace and screen, are also important but represent a much smaller share of the market. Table 6-1 presents current and future trends in the distribution of printing processes. Since offset lithography and gravure are the most popular printing processes used, they will be discussed in greater detail in this report. Detailed discussion of the other printing processes may be found in the literature (USEPA 1976). Figure 6-1 is a block flow diagram of offset lithography and gravure printing operations.

Table 6-1 Trends in Distribution of Printing Processes in the U.S.

Process	Year			
	1977	1985	1990	1995
Lithography	38%	45%	47%	46%
Gravure	14%	18%	20%	21%
Letterpress	32%	15%	8%	4%
Flexography	11%	16%	18%	21%
Screen printing and other processes	5%	6%	7%	8%

Source: Profit from Pollution Prevention (Campbell and Glenn 1982); Status of Printing in the USA (Bruno 1985).

Except for the use of a plate or cylinder to transfer ink to a substrate (such as paper) both off-set lithography and gravure are conceptually very similar. Art work or copy is prepared and the image is transferred to the plate or cylinder. This operation makes certain areas of the plate or cylinder receptive to ink (the image area). The substrate is then passed by the plate (i.e. the ink is first tranferred from the plate to a rubber blanket, and then onto the substrate) or cylinder. The substrate absorbs the ink, thus reproducing the image. The substrate is then processed mechanically (cut, folded, bound, etc.) to produce the final product. Since the only major difference between lithography and gravure lies in the manner in which the plates or cylinders are made and subsequently operated, the following discussion will be general except where further details are warranted.

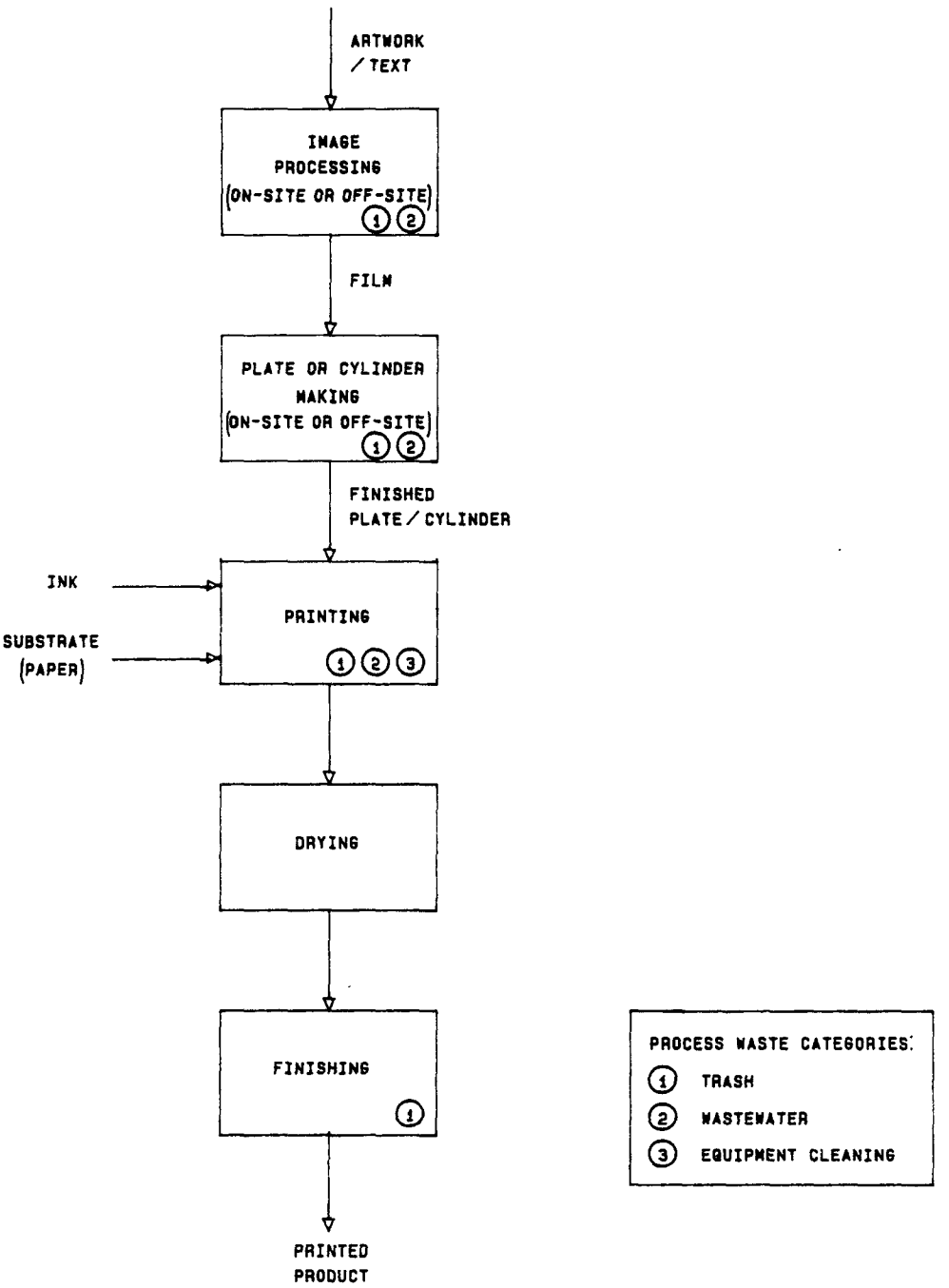


Figure 6-1 Block Flow Diagram for Offset Lithography / Gravure Printing Operations

Most printing operations begin with art and copy (or text) preparation. Once the material is properly arranged, it is photographed to produce transparencies and color separations. Color separations are required to provide a single-color image or record which can then be used to produce the single-color printing plate for lithography or the cylinder for gravure (multi-color printing is done by passing the substrate through several single-color printing operations). Once the film has been developed, checked, and rephotographed (if necessary), it is sent on to the plate- or cylinder-making operation.

Plate making consists of cleaning or counter-etching the surface of an aluminum plate and then applying a photosensitive coating. Counter-etching involves the use of dilute acid solutions such as phosphoric, acetic, hydrochloric, and sulfuric acids, although alkaline counter-etches are sometimes employed. The solution is poured on the surface and agitated with a bristle brush. The plate is then copiously rinsed with water. The metal surface is then coated in the whirler with a photosensitive solution consisting of an aqueous solution dichromate, ammonium hydroxide, and colloidal protein.

The image from a photolithographic negative is transferred to the photosensitive plate by exposure to light, and the coating is covered with a developing ink to increase the affinity of the image area for ink during printing. The plate is developed by removing the unhardened non-image areas of the coating with dilute ammonium hydroxide solution and is then washed with water and dried. An acidified solution of gum arabic, which may also contain ammonium dichromate, is subsequently used to desensitize the developed plate. Finally, the plate is again washed with water, a plain solution of gum arabic is applied, and the plate is allowed to dry.

Cylinder making begins with a steel cylinder plated with copper. The cylinder is machined and polished so as to remove any imperfections in the copper plating. Next, the surface is either engraved using a diamond stylus or chemically etched using ferric chloride. Use of ferric chloride requires that a resist (in the form of the negative image) be transferred to the cylinder before etching. The resist protects the non-image areas of the cylinder from the etchant. After etching, the resist may be subsequently stripped off. This operation is analagous to the manufacturing of

printed circuit boards. Following this operation, the cylinder is proofed or tested, re-worked if required, and then chrome plated.

Following the plate- or cylinder-making operation, the next step is printing. In lithographic printing, the plate is mounted to a rotating cylinder. As the cylinder rotates, a dampening solution followed by ink is transferred to the plate's image area. The inked image repels the solution and accepts the printing ink, while the non-image area accepts the dampening solution and repels the ink. As the cylinder continues to rotate, the inked image is transferred to a rubber roller or blanket and then onto the substrate. The two major forms of substrates used in lithography are single sheets of paper, (sheet-fed lithography) and continuous rolls of paper (web lithography).

In gravure printing, the cylinder is placed in the press and partially immersed in an ink bath or fountain. Solvent is added to the ink to maintain the proper level and viscosity of the bath. As the cylinder is rotated, ink coats the entire surface. Next, a metal wiper (doctor blade) presses against the surface of the cylinder and removes ink from the non-etched (non-image) areas. The substrate is then pressed against the rotating cylinder and the ink is transferred.

After printing, the substrate may pass through a drying operation depending on the type of ink used. Lithography can use heat-set and non-heat-set inks. In heat-set lithography, the substrate is passed through a tunnel or floater dryer which utilizes hot air or direct flare. With non-heat-set lithography, the ink is normally air dried. Gravure uses heat-set inks, so a drying operation is required. Following this drying operation, the printed substrate can be finished by slitting, cutting, trimming, folding, binding, laminating, or embossing.

7. WASTE DESCRIPTION

Listed in Table 7-1 are the principal wastes associated with lithographic printing operations. Gravure printing operations have been excluded since the major difference between the two processes, from a waste generation viewpoint, is in the plate- and cylinder-making operation. Gravure cylinder making is very similar to other metal

Table 7-1 Offset Lithography Printing Process Wastes

Waste Stream No	Waste Description	Process Origin	Composition	RCRA Codes
1.	Trash	Image Processing	Empty containers, packages, used film, out-dated materials	----
		Plate Making	Damaged plates, developed film, out-dated materials	----
		Printing	Test production, bad printings, empty ink containers, used blankets	----
		Finishing	Damaged products, scrap	
2.	Wastewater	Image Processing	Photographic chemicals, silver	----
		Plate Making	Acids, alkali, solvents, plate coatings (may contain dyes photopolymers, binders, resins pigments, organic acids), developers (may contain isopropanol, gum arabic, lacquers, caustics), and rinsewater.	F002 F003 F005
		Printing	Spent fountain solutions (may contain chromium).	----
3.	Equipment Cleaning Wastes	Printing	Lubricating oils, waste ink, clean up solvent (halogenated and non-halogenated), rags.	F002 F003 F005

processing operations; therefore, the reader is referred to the process studies on metal parts cleaning, electroplating, and metal surface treatment elsewhere in this appendix for information regarding the types of waste that would be encountered. Additionally, the inks used by the gravure industry tend to contain solvent and heavy metals, unlike the inks used by the lithographic industry*. While this would affect the ways in which certain wastes are classified, regulated, handled, and disposed, the nature of the inks used for lithography does not detract from the desirability of minimizing all non-paper waste.

The major wastestream encountered in the lithographic industry is trash. Almost 98 percent of the total waste generated by this segment of the industry is spoiled paper and paper wrap*. This paper is normally recycled, incinerated, or disposed of. Other trash, such as scrap photographic material, is sold for metal recovery. Empty containers are normally scraped clean of ink (to an economically feasible extent) and discarded.

Wastewater from image processing is normally treated to recover silver and is then discharged. Plate-making wastes, such as acids and alkalis used to clean the plates, must be either sent to wastewater treatment or drummed for disposal. For facilities that use pre-sensitized plates, this waste is avoided (though the supplier of the pre-sensitized plates would be producing this waste). Currently, only large-volume users of plates (i.e. newspapers) still produce their own plates*. Photochemical wastes would be handled in the same manner as image processing wastes. Wastewater containing spent fountain solutions may go to a waste treatment unit but is normally discharged into the sewer.

The final wastestream, equipment cleaning wastes, consists of dirty rags soaked with solvent and waste ink. Dirty rags are laundered, are disposed as trash, or are incinerated. If a facility employs a professional laundry, then the rags are picked up, laundered, and returned. The fate of the solvent and ink contained in these rags would depend on how the laundry is designed and operated (e.g. water vs. dry cleaning). Most waste inks are either incinerated or discarded with the trash.

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* Graphic Arts Technical Foundation 1985: Personal communication.

8. WASTE GENERATION RATES

The only published estimates of the nationwide waste generation rates from the graphic arts industry were given for 1972 (Bohn 1976). It was estimated that the industry as a whole generated 7,300 short tons of waste excluding waste paper and photoprocessing chemicals. Separate listings by type of operation analyzed were not provided and more recent estimates have not been reported. Fractional waste generation rates for the lithographic printing industry were estimated by project staff based on the available information, engineering judgement, and input from the industry. These values, excluding trash attributable to scrap or waste paper, are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

The list of individual primary lithographic waste streams and their sources along with a list of source reduction methods is presented in Table 9-1. Recommended waste reduction methods and identified procedures are discussed in the following sections. The basis for identification came from published accounts in the open literature and industry contacts.

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" has also been included. Good operating practices are defined as procedures or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practices:

- Waste stream segregation
- Personnel practices
  - Management initiatives
  - Employee training
- Procedural measures
  - Documentation
  - Material handling and storage
  - Material tracking and inventory control
  - Scheduling

- Loss prevention practices
  - Spill prevention
  - Preventative maintenance
  - Emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Trash

Even excluding spoiled paper, trash represents a major wastestream in the lithographic industry. This wastestream includes used photographic film, empty containers and packages, and out-dated materials. The following waste reduction measures were noted:

- Recycle empty containers.
  Most ink containers are scraped free of ink and discarded in the trash. Since the degree of cleanliness is a function of operator effort, the amount of ink discarded can vary widely. By purchasing ink in recyclable bulk containers, the container can be returned to the ink supplier for refilling instead of being thrown away. In addition, the use of bulk containers also cuts down on the amount of cleaning required since the surface area of the container per unit volume of ink stored is reduced.

- Recycle spoiled photographic film and paper.
  It is already a current practice of the industry to send used and/or spoiled film to professional recyclers for recovery of silver*. However, this option might not be practical to small scale producers or available to facilities located far away from recyclers.

- Electronic imaging and laser platemaking.
  Since all text and photos are edited on a video terminal, the need for photographing, editing, and re-shooting is reduced. In addition, color separations can be produced electronically and therefore may eliminate the need for the many photoprocessing steps currently employed.

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* R.R. Donnelley & Sons 1985: Personal communication.

- Installation of web break detectors.
  The Oxy-Dry Corporation manufactures an electronic system that detects web breaks in a non-contact fashion that will neither smear ink nor crease the web, thereby reducing waste from these sources. Both McGraw-Hill Publications in New York, New York, and the St. Petersburg Times in St. Petersburg, Florida have installed web break detection systems and have reduced waste (Campbell and Glenn 1982).

- Monitoring press performance.
  Crosfield in Chicago, Illinois, markets the Pressdata 190 waste system which provides a means of monitoring press performance.

- Better operating practices.
  Photosensitive film and paper storage areas should be designed for economical and efficient use. Some shops waste up to one-fourth of these materials due to improper storage (op. cit.)

9.1.2 Wastewater

Wastewater comes from two main sources: image processing (including plate developing) and the platemaking process. Other sources are clean-up operations and spent formation solutions. Since these wastes are produced by many different processes and therefore require different minimization procedures, each operation is discussed separately.

Image processing (and plate developing) The photographic industry has made great strides in pollution abatement and many of the methods developed by this industry are applicable to the printing industry. The waste reduction methods are as follows:

- Use silver-free films.
  Napp Systems, among several other companies, is marketing silver free films for lithography (Campbell and Glenn 1982).

- Use water-developed lithographic plates.
  3M is marketing its Hydrolith plate which requires only water to process aluminum off-set plates (op. cit.).

- Electronic imaging and laser platemaking.

  Text and photos are read by an electronic scanner, edited with a display monitor, and non-silver plates are made using laser beams*. Due to the expense of this system, it is currently being tried by only the largest of printers, e.g. newspapers. USA Today currently employs this system.

- Recover silver and recycle spent chemicals.

  Basically, photoprocessing chemicals consist of developer, fixer, and rinse water. Keeping the individual process baths as uncontaminated as possible is a prerequisite to the successful recycling of these chemicals. Silver is a component in most photographic films and paper and is present in the wastewaters produced. Various economical methods of recovering silver are available (e.g. metallic replacement, chemical precipitation, electrolytic recovery) and a number of companies market equipment that will suit the needs of even the smallest printing shop. Technologies for re-use of developer and fixer are available. These technologies make use of various methods such as ozone oxidation, electrolysis, and ion exchange.

- Employ counter-current washing.

  Counter-current washing, as opposed to the parallel tank system, reduces processing solution contamination thereby increasing the ease of recycling process baths and reducing the quantity of make-up chemicals required. In a parallel system, fresh water enters each wash tank and effluent leaves each wash tank. In counter-current rinsing, water from previous rinsings is used in the initial film-washing stage. Fresh water enters the process at the final rinse stage, at which point much of the contamination has already been rinsed off the film. The main consideration in a counter-current system is availability of space.

- Use of squeegees.

  Squeegees in non-automated processing systems can reduce chemical carry-over typically by 50 percent on film and paper from one process bath to the next by wiping off excess liquid. Minimizing chemical

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* Printing Industries Association 1985: Personal communication.

contamination of process baths increases ease of recycling, enhances the lifetime of the process baths, and substantially reduces the amount of replenisher chemicals required. Most firms, however, use automated processors*.

- Better operating practice.
  Taking care to accurately add and monitor chemical replenishment of process baths will cut down chemical wastage. Some process chemicals have expiration dates. If there are not enough orders to consume these chemicals before they expire, these would go to waste. Pre-mature expiration of light-sensitive chemicals may be prevented by keeping them in the dark.

  Easily oxidizable process baths may be protected from quickly losing potency by reducing their exposure to air. Small-scale photo developers store their chemicals in closed plastic containers and use glass marbles to bring the liquid level to the brim each time liquid is used. This way, the amount of oxygen available to the chemical is reduced to a minimum, thereby extending the chemical's useful life.

Wastewater from platemaking Only the newspaper sector of lithography still widely employs platemaking. Waste reduction can be accomplished using the following technique:

- Removal of heavy metals from wastewater.
  Hexavalent chromium can be reduced to the less toxic trivalent form by lowering pH to about 2 with a strong mineral acid and then adding a strong solution of reducing agent such as ferrous sulfate or sodium bisulfite. Upon addition of caustic soda or lime, the heavy metals will precipitate out as hydroxides (Latus 1976). This is applicable to older technologies that are being phased out but would not apply to newer systems**. Moreover, hooking up holding tanks to the sink and whirler will prevent the pollutants from reaching the municipal sewage system without prior treatment.

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* R.R. Donnelley and Sons 1985: Personal communication.
** Printing Industries Association 1985: Personal communication.

9.1.3 Clean-up Solvents and Waste Ink

The clean-up solvent waste stream consists of waste ink, ink solvents, lubricating oil, and solvent. In many printing establishments, excess ink and solvent is collected in a drip pan underneath the press. This waste is typically drummed and hauled away to a landfill area. The following waste reduction methods are noted:

- Recycle waste ink and clean-up solvent.
  Ink recovery machines are commercially available in a number of sizes. For firms which choose not to recycle waste ink onsite, it can be sent back to the ink manufacturer who may turn it into black newspaper ink (Campbell and Glenn 1982, Huisingh et al. 1985).

  If waste cleaning solvent is generated in substantial quantity, it may be recycled on-site or sent to a professional solvent recycler. In many cases, however, a printing shop does not generate enough solvent waste to justify onsite recycling. Waste solvent can be reclaimed through simple batch distillation or can be incinerated with recovery of heating value.

  Clean-up is usually done by wetting a piece of rag with solvent and wiping the equipment to be cleaned, or by pouring some solvent on the equipment and wiping it. Drip pans are placed underneath equipment to collect waste solvent. The dirty rags are then sent to professional cleaners for cleaning or drummed for disposal. In many cases, the nature of the waste does not lend itself readily to recycling efforts. However, as indicated by the example of better operating practice given below, waste handling procedures can often be changed to facilitate recycling.

- Use of automatic cleaning equipment can promote a more efficient use of cleaning solvent*. However, this equipment is very expensive to purchase and maintain.

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* R.R. Donnelly and Sons 1985: Personal communication.

- Use of an automatic ink leveller.
  Oxy-Dry Corporation is one company that produces this equipment which maintains the desired ink level in the fountain for optimum inking conditions. This prevents ink waste and ink spoilage around the press (Campbell and Glenn 1982).

- Substitution with less toxic solvent.
  In some cases it may be possible to substitute highly toxic aromatic solvents, such as benzene or toluene, with less toxic straight chain paraffinic solvents, e.g. hexane.

- Better operating practices.
  Rexham Corporation of Matthews, N.C., does high-tech printing and coating, including film substrate, for the photographic industry. Toluene is used to clean the ink from the press, and runoff toluene is collected as waste. Rexham has nearly eliminated its toluene waste by segregating used clean-up toluene according to the color and type of ink contaminant and then reusing the collected wastes to thin future batches of the same ink. The procedure has no effect on product quality and has resulted in almost 100% reuse of the toluene solvent (Huisingh et al. 1985).

9.2 Implementation Profile

Most of the measures undertaken by the printing industry to reduce waste center around recycling of materials and the implementation of good operating practices. The technical and commercial viability of recycling waste ink is evidenced by the commercial availability of ink recovery machines. Portable and non-portable models are available to suit the different needs and preferences of printers. For waste ink that is contaminated, turning it into black newspaper ink may be more practical than preserving the original color. Implementation of good operating practices either assures that materials can be more readily recycled or avoids the need for recycling altogether.

The installation of silver, ink, and/or solvent recovery equipment (among other methods) requires significant capital outlays and entails possible increases in labor costs. The economic feasibility of making these changes depends in large measure upon the quantity of recoverable/recycleable material generated by a facility. Small-volume waste ink generators may find internal or on-site recycling less economical than sending their ink runoff to ink manufacturers who can convert it into black newspaper ink or to recyclers who collect from groups of small-volume generators. Large-volume generators, who comprise approximately 20 percent of all waste ink generators, will likely find on-site recovery systems to be more cost-effective. The availability of greater financial and personnel resources serves to enhance the potential for cost-effective on-site recovery and recycling for large-volume generators.

9.3 Summary

The sources of waste from the conventional lithographic printing process and the associated source control techniques are summarized in Table 9-1. Spoiled paper and paper wrap were excluded from this summary so as to provide a better focus on the wastes of concern. The ratings listed in the table are based on a scale of 0 to 4 and are used to evaluate each technique for its waste reduction effectiveness, extent of current use and future application potential. The ratings were derived by project staff from the available information and from industry comments.

It appears that the current level of waste minimization in the lithographic printing industry is high. This is evidenced by the current reduction index (CRI) of 2.5 (63 percent) which measures the extent of reduction in the waste that otherwise would be generated if none of the listed methods were applied as they are currently.

The potential for future reductions appears modest to significant, as evidenced by the future reduction index (FRI) of 0.7 to 1.4 (18 to 35 percent). The future reduction index is the measure of waste reduction achievable through implementation of the listed techniques to their full rated potential.

Ways in which these reductions can be achieved would be to recycle empty ink containers and increase the use of counter-current rinsing and good operating practices. Measures that have helped the industry to achieve a high degree of

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE PRINTING OPERATIONS INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Trash	1. Recycle empty containers	0	0	3	0	2		0.0	1.5	1.5
	2. Recycle spoiled photographic film	1	1	3	3	1		2.3	0.2	
	3. Electronic imaging/laser platemaking	1	1	2	1	2		0.5	0.8	
	4. Install web break detectors	1	1	1	1	2		0.3	0.4	
	5. Monitor press performance	1	1	1	1	2		0.3	0.4	
	6. Better operating practices	1	1	2	1	4		0.5	1.5	1.5
	Overall	0.83	0.83	2.00	1.17	2.17	0.36	2.3	0.8	1.5
Wastewater	1. Use silver free films	1	1	1	1	1		0.3	0.2	
	2. Use water developed litho plates	1	1	4	3	2		3.0	0.5	
	3. Electronic imaging/laser platemaking	1	1	2	1	2		0.5	0.8	
	4. Recover silver and recycle chemicals	1	1	4	3	1		3.0	0.3	
	5. Use counter-current washing sequence	1	2	4	2	2		2.0	1.0	
	6. Use of squeegees	1	1	1	1	1		0.3	0.2	
	7. Better operating practices	1	1	2	2	3		1.0	0.8	
	8. Remove heavy metals from wastewater	1	2	3	1	2		0.8	1.1	1.1
	Overall	1.00	1.25	2.63	1.75	1.75	0.24	3.0	0.6	1.1
Clean-Up Solvent and Waste Ink (*)	1. Recycle waste ink and solvent	2	2	2	2	3		1.0	0.8	
	2. Use of automatic cleaning equipment	1	1	2	1	1		0.5	0.4	
	3. Recovery of heating value from waste	1	1	4	1	1		1.0	0.8	
	4. Use of an automatic ink leveller	1	1	1	1	2		0.3	0.4	
	5. Use less toxic solvent	0	0	0	2	2		0.0	0.0	
	6. Better operating practices	2	2	4	2	3		2.0	1.5	1.5
	Overall	1.17	1.17	2.17	1.50	2.00	0.40	2.0	0.6	1.5
All Sources	All Methods						1.00	2.5	0.7	1.4

(*) These waste streams include listed "F" and/or "K" RCRA wastes.

reduction (but appear to have limited potential for further implementation) include recovery of silver from film and process solutions and switching to water-developed lithographic plates.

10. SUBSTITUTION ALTERNATIVES

10.1 Ink Substitution

Conventional inks used in lithography are heat-set solvent-base inks which contain coloring pigments and about 30 to 60 percent low boiling organic solvents. Most of the solvent is removed during the drying step and is either emitted into the air, recycled, or incinerated. New types of ink are described below. These were formulated with air pollution reduction (particularly solvent emissions reduction) and energy conservation as a goal.

- Water-base inks.
  Also called water-borne inks, these inks are usually pigmented suspensions in water. These inks find their greatest application in flexographic printing on paper substrates (Campbell and Glenn 1982) and their use is also recommended for gravure* (water-base inks are not available yet for lithography).

  One factor stifling the development of water-base inks is that they require more energy to dry than do solvent-borne inks. Another difficulty results from the necessity to shut presses down for short periods of time. During this period the ink dries, and since water is not a solvent for the dried ink, more frequent equipment cleaning is required. Other problems besetting water-borne inks are low gloss and paper curl.

- UV-cured inks.
  These inks consist of one or more monomers and a photosynthesizer that selectively absorbs energy. Benefits of using UV inks are that the inks contain no solvent. The paper is not heated above 50° C, and a minimum of moisture is lost in the process (Carpenter and Hilliard 1976, Shahidi and

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* National Printing Ink Research Institute 1985: Personal communication.

Rowanda 1975, Bassemir 1974). Since the inks do not "cure" until exposed to UV light, and may therefore be allowed to remain in the ink fountains (and plates) for long periods of time, the need for clean-up is reduced. UV inks are particularly attractive for letterpress and lithography applications. The following have been cited as advantages of using UV inks for sheet-fed lithography (Carpenter and Hilliard 1976):

- Elimination of "set-off", the unintentional transfer of ink to adjacent sheets before the ink has dried up completely.

- Elimination of the use of powders that are applied to protect an ink film that is "set" but not "dry".

- Elimination of the storage of printed sheets for ventilation required in oxidative drying processes.

The disadvantages of the UV-cured inks include:

- Cost (75 to 100 percent more expensive than conventional heat-set inks).

- Hazards of UV to operating personnel.

- Formation of ozone by the action of UV light on oxygen.

- Conventional commercial paper recycling process will not remove the UV-cured ink which hinders recyclability of the paper printed with this method.

- Some chemicals used to formulate the ink are toxic.

o Electron-beam-dried (EB) inks.

The "low-energy" EB system was developed by Energy Sciences Inc., of Bedford, Massachusettts. Electri Graphics markets the Electricure system

which is claimed to operate at a much lower energy than the EB system. Many advantages are claimed over the use of conventional heat-set ink and other curing systems (Perino 1976, De Young 1976). Like UV curing, EB curing causes resins to crosslink. Inks can be applied as fluid monomers and rapidly converted to tough, solid polymers. The fluidity of the resin eliminates the need for solvent. UV ink can be converted to EB-curable, but little has been done to develop EB-curable coatings for use where UV does not appear practicable. The disadvantage in EB systems is the degradation of paper and the generation of x-rays that necessitates elaborate and expensive operator protection (Carpenter and Hillard 1976, Anonymous 1975).

- Heat-reactive inks.

  These inks contain a pre-polymer, a cross-linking resin, and a catalyst. The catalyst activates at 350°F in the dryer and converts the liquid into a solid polymeric film via condensation polymerization reactions. Reaction by-products are principally C_1-C_4 alcohols, moisture, and small amounts of formaldehyde. Overall volatile content of these inks is 20 percent or less of that of the conventional heat-set inks. The smoking tendency was reported to be practically nil. Because heat is required for drying, these inks cannot be used on sheet-fed presses. Moreover, they are reported to permit build up of static electricity in the folding operation (Carpenter and Hillard, 1976).

10.2 Equipment Substitution

- Electrostatic screen printing process.

  Also known as pressureless printing, this process was developed by the Electrostatic Printing Corporation of America and therefore is called the EPC process (USEPA 1979b). A thin, flexible printing element, with a finely screened opening defining the image to be printed, is used. An electric field is established between the image element and the surface to be printed. Finely divided "electroscopic" ink particles, metered through the image openings, are attracted to the printing surface, where they are firmly held by electrostatic forces until they have been fixed by heat or by chemical means.

Other alternatives to conventional printing include "desk-top" publishing using micromputers with laser printers - development seen by some as presenting a serious future competition to small printing shops.

11. CONCLUSIONS

The industry has significantly reduced non-paper waste as evidenced by a current reduction index of 2.5 (63 percent). Estimates indicate that future waste reductions are expected to be moderate as characterized by a future reduction index of 0.7 to 1.4 (18 to 35 percent). Several methods that appear to be quite effective for the industry as a whole include implementation of better operating practices, recycling of empty ink containers, and the continued or increased recycling of silver, solvent, and waste ink. For those waste reduction measures that could be used by the gravure industry to reduce waste due to their electroplating operations, the reader is referred to the process studies on electroplating, metal parts cleaning, and metal surface finishing.

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13. INDUSTRY CONTACTS

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1. PROCESS: SYNTHETIC FIBERS MANUFACTURE
2. SIC CODE: 2824
3. INDUSTRY DESCRIPTION

By definition, SIC 2824 includes establishments involved in the production of synthetic (or more commonly called man-made) noncellulosic organic fibers. Cellulosic fibers such as acetate and rayon and the noncellulosic inorganic fibers such as boron, fiberglass, and graphite are excluded. Included in SIC 2824 are acrylic and modacrylic fiber, nylon, olefin (such as polyethylene and polypropylene), and polyester. These four fiber types comprise more than 99 percent of the total man-made fiber produced in the United States (Farr 1977).

The manner in which fiber production is carried out involves a small degree of integration between fiber producer and user. Fiber production begins with the production of a polymer solution and ends with the packaging and shipment of the fiber to a convertor or downstream processor. It is the convertor or downstream processor who twists the fiber into cord, dyes it, weaves it, and knits it. Fiber manufacturers who do not produce their own polymer purchase it in flake or pellet form from a supplier. However, the majority of fiber producing operations are fully integrated with the polymerization operation.

3.1 Company Size Distribution

In the U.S., synthetic fibers are currently produced by 28 companies which own and operate a total of 71 facilities. The synthetic fiber industry employs approximately 60,000 people (USDC 1985).

3.2 Principal Producers

Table 3-1 lists the ten largest producers of synthetic fibers and their major products. These ten companies account for about 85 percent of the total capacity of organic man-made fibers in the United States.

Table 3-1 Major U.S. Producers of Man-Made Organic in Fibers in (1981)

Producer	Major Products and Capacities (millions lb/yr.)			
	Acrylic	Nylon	Olefin	Polyester
Akzona Inc.	--	210	15	147
Allied Chemical Corp.	--	455	--	80
American Hoechst Corp.	--	--	--	460
Badische Corp.	70	145	--	--
E.I. du Pont de Nemours & Co., Inc.	317	1375	--	1623
Eastman Kodak Co.	40	--	--	540
Fiber Industries Inc.	--	--	--	1406
Hercules Incorporated	--	--	130	--
Monsanto Co.	315	560	--	120
Standard Oil Co. (Indiana)	--	--	215	--
Total	742	2745	360	4376

Source: Chemical Economics Handbook (SRI 1982).

3.3 Geographical Distribution

Of the 71 plants in operation in 1982, 44 were located in the states of North Carolina, South Carolina, Virginia, and Tennessee (USDC 1985). The remaining 27 plants were located in several adjoining states such as Georgia, Alabama, and Maryland. These fiber producers are mostly concentrated in EPA regions III and IV. Figure 3-1 depicts a geographical distribution of these producers.

4. PRODUCTS AND THEIR USE

Man-made fibers are broken into two major categories which can be further subdivided as shown below:

Man-made
- cellulosic
  - acetate
  - rayon
- noncellulosic
  - inorganic
  - organic

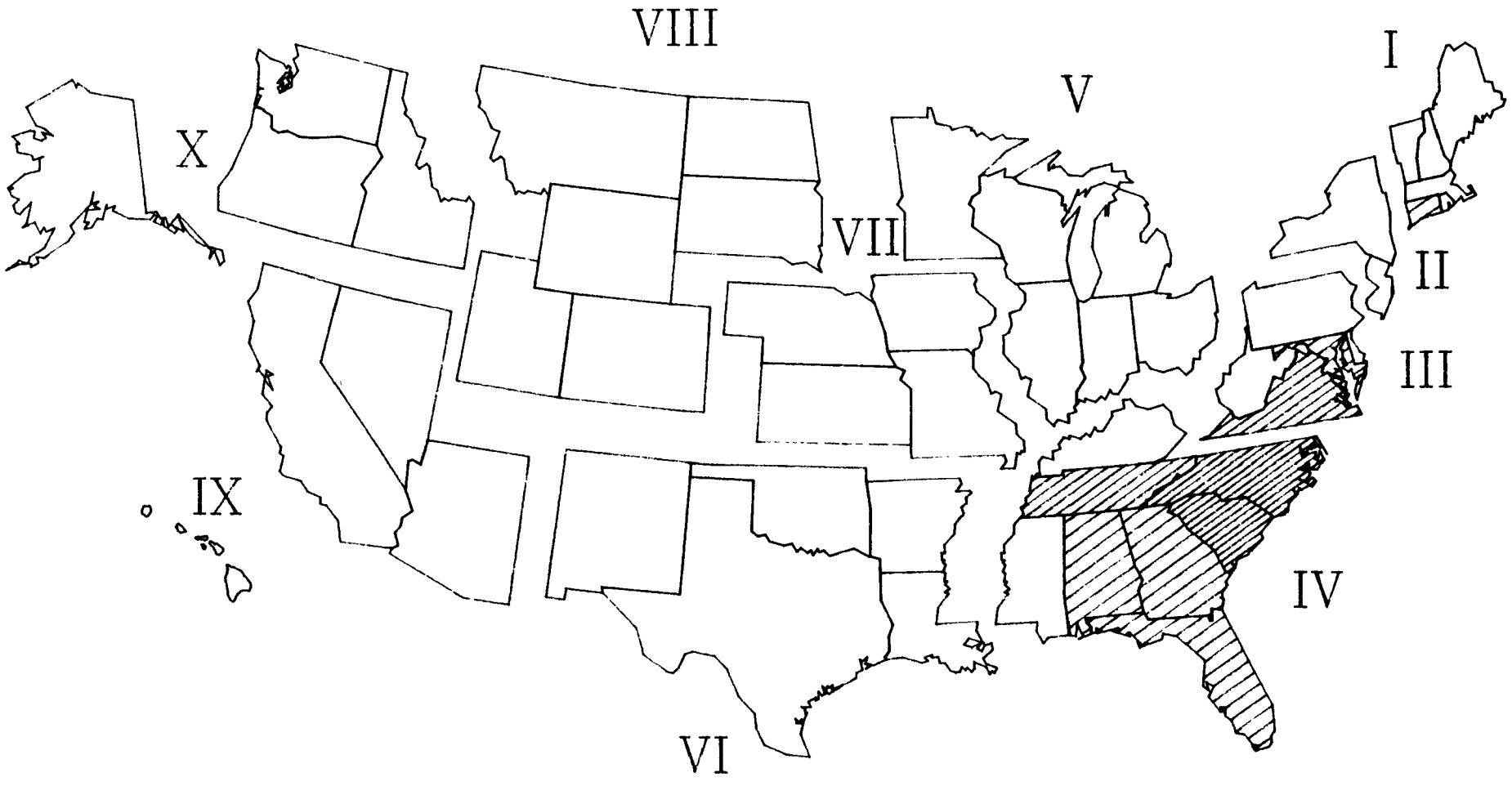

Figure 3-1 Synthetic Fiber Plants in the U.S.

Noncellulosic organic fibers (SIC 2824) include acrylic and modacrylic fiber, nylon, olefin, and polyester. Modacrylic fiber is composed of at least 85% by weight acrylonitrile. Nylon is a polyamide in which less than 85% of the amide linkages are attached directly to two aromatic rings. Olefin is composed of at least 85% by weight ethylene, propylene, or other olefins. Polyester is composed of at least 85% by weight of an ester of a substituted aromatic carboxylic acid (including but not restricted to substituted terephthalate units and parasubstituted hydroxy-benzoate units).

Fibers are generally marketed as yarn, staple, or tow. Other forms are monofilament, split film, fiberfill, and nonwoven fabrics. The major end uses of man-made fibers are shown in Table 4-1. About half of the synthetic fiber produced goes into the making of knit and woven apparel, about 30 percent goes for home furnishings, and the remainder for various industrial uses. Over 80 percent of the fiber used in home furnishings is for rugs, carpets, and carpet backing. Most of the remainder is used for draperies and upholstery. The major industrial use of man-made fibers is for automobile tire cord. Other uses of these fibers are automobile seat covers, belting, electrical wire insulation, hose, recreational surfaces, roofing, rope and twine, sewing thread, tents, parachutes, sails, tarps, and webbing for outdoor furniture.

5. RAW MATERIALS

Relatively pure raw materials are required to produce man-made fibers because of the deleterious effect of impurities on the properties of the fiber. The monomers (described above) are derived from basic petrochemicals such as benzene, butadiene, ethylene, propylene, and xylene. Table 5-1 presents a list of monomers and other intermediate products from which the fiber-forming polymers are produced.

Many additives are blended with the polymer before fiber production. Examples are delustrants, pigments, dyeing assistants, dye receptors, optical brighteners, heat stabilizers, antioxidant stabilizers, and light stabilizers. Ordinarily, the total amount of additives does not exceed five percent. Materials added to the fiber to enhance product utility include lubricating agents, bacteriostats, humectants, anti-static agents, and other additives. Table 5-2 contains a list of some additives added to man-made fibers to increase their usefulness.

Table 4-1 Synthetic Fiber Product and Their Use in million lbs./yr.

	Acrylic/ Modacrylic	Nylon				Polyester			Polyolefin		
	Staple and Tow	Filament, Monofilament	Textured Yard	Stable and Tow	Total	Filament, Texturized Yarn	Stable and Tow	Total	Yarn, Mono filament and Fiber Film	Stable and Tow	Total
Apparel	467	383	149	17	549	1,667	1,096	2,763	11	--	11
Knit	461	324	147	3	474	1,054	318	1,372	11	--	11
Woven	6	59	2	14	75	613	778	1,391	--	--	--
Home Furnishing	111	740	12	659	1,411	152	513	665	326	77	403
Carpets/Rugs	n.a.	715		632	1,347	--	120	120	287	62	349
Curtains and Draperies	14	1		--	1	62	48	110	--	--	--
Upholstery	9	24		25	49	13	10	23	39	15	54
Other	88	1	12	2	15	77	335	412	--	--	--
Industrial	7	366	6	35	407	310	461	771	275	38	313
Rubber Industry	--	232	2	--	234	191	--	191	1	--	1
Nonwovens	1	1		13	14	1	150	150	31	35	66
Rope and Cordage	--	28	1		29	13	2	15	84	--	84
Fiberfill	1	--	--	--	--	--	205	205	--	--	--
Other	5	105	3	33	130	105	309	414	159	3	162
Total	585				2,367			4,199			727

Source: Chemical Economics Handbook (SRI 1982).

Table 5-1 Input Raw Materials for Production of Organic Man-Made Fibers in 1982

Raw Material	Consumption million lb/yr
Acrylonitrile	743
Caprolactam (nylon 6)	840
Adipic acid + hexamethylenediamine (nylon 6,6)	1860
Glycols (ethylene, propylene, etc.)	1362
Dimethyl terephthalate (DMT)	1560
Terephtalic acid (TPA)	1386

Source: 1982 Census of Manufacturers (USDC 1985).

Table 5-2 Typical Additives Used in Organic Man-Made Fiber Production

Delustrants	Usually titanium dioxide
Optical brighteners	Stilbene Phenyl coumarin derivatives
Antioxidant stabilizers	Alkylated phenols p-cresols mixed with sulfides Thio compounds such as dilauryl or distearyl thio dipropionate
Light stabilizers	Long-chain alkyl derivatives of hydroxybenzophenones
Dyeing assistants	2-methyl 5-vinyl pyridine 2-vinyl pyridine p-vinyl-benzene sulfonic acid sulphocinamic acid
Lubricants and other finishes	Polyoxyethylene attached to aliphatic hydrocarbon Long-chain alkyl quartenary ammonium salts Hydroxyalkyl amine salts of fatty acids Aliphatic esters Hydrocarbons Fluid silicones

Source: Industrial Process Profiles for Environmental Use (Farr 1977).

For some fibers, solvents are mixed with the polymer in order to obtain a liquid solution amendable to fiber formation. These solvents invariably are recovered and recycled. Solvent is almost exclusively used for the production of acrylics and modacrylics. The most widely used solvents are dimethylacetamide, dimethylformamide, acrylonitrile, acetone, aqueous $ZnCl_2$, aqueous NaSCN, tetramethylene sulfane.

6. PROCESS DESCRIPTION

Man-made fibers are formed primarily by three different processes: melt spinning, wet solution spinning, and dry solution spinning. Wet and dry solution spinning are used for producing acrylic and modacrylic fibers. Melt spinning is used for producing nylon, polyester, and polyolefin fibers. A summary of production methods for acrylic/modacrylic fibers is given in Tables 6-1 and 6-2.

Table 6-1 Acrylic Fiber Processes

Spinning process	Solvent	World capacity, %
Dry	Dimethylformamide	22
Wet	Dimethylformamide	11
Wet	Dimethylacetamide	23
Wet	Aqueous NaSCN	23
Wet	Aqueous HNO_3	12
Wet	Aqueous $ZnCl_2$	4
Wet	Dimethyl sulfoxide	3
Wet	Ethylene carbonate	2

Source: Kirk-Othmer Encyclopedia of Chemical Technology, 3rd. Ed. (Roberts 1980)

Table 6-2 Acrylic and Modacrylic Fiber Production Routes

Company	Registered Trade Name	Typical Chemical Composition of Fiber	Polymerization Medium	Type of Polymerization Operation	Type of Spinning Process	Spinning Solvent
Acrylic Fibers						
American Cyanamid Company	Cresland	89-90% Acrylonitrile 8% Methyl Methacrylate	Solution	Continuous	Wet	Aqueous NaSCN
Dow Badische Company	Zefran	87-90% Acrylonitrile 8% Methyl Acrylate 2-5% Other	Solution	Continuous	Wet	Aqueous $ZnCl_2$
E.I. du Pont de Nemours & Company, Inc.	Orlon	88-91% Arcylonitrile 7% Methyl Acrylate 2-5% Other	Suspension	Continuous	Dry	DMF
Monsanto Company	Acrilan	88-91% Acrylonitrile 8-10% Vinyl Acetate 2-4% Other	Suspension	Batch	Wet	DMAc
Modacrylic Fibers						
E.I. du Pont de Nemours & Company, Inc.	Orlon FLR	66-70% Acrylonitrile 30% Vinyl Chloride 0-4% Other	Suspension	Continuous	Dry	DMF
Eastman Chemical Products, Inc.	Verel	37% Acrylonitrile 40% Vinylidene Chloride 20% Isopropylarcylamide 3% Methyl Acrylate	Solution	Batch	Dry	Acetone
Monsanto Company[a]	Elura	76-78% Acrylonitrile 20% Vinyl Acetate 2-4% Other	Suspension	Batch	Wet	DMAc
	SEF	79-81% Acrylonitrile 8% Vinylidene Chloride 9% Vinyl Bromide 2-4% Other	Suspension	Batch	Wet	DMAc

Source: (SRI 1982).

[a]In addition, Monsanto also has two other modacrylic fibers, known as type 65 and type 67.

Fiber production begins with the production of polymer in a polymerization reactor. This reactor can be operated either in a batch or continuous mode depending on the type of polymer being produced. The major route for polymerization of acrylonitrile is as a water emulsion. Most of the water formed is subsequently used in other operations. By-products of polymerization also occur with the manufacture of nylon 6,6 and polyester. Most of these by-products also find use in other parts of the process. For many other polymers, no by-products are formed.

The choice of spinning method employed depends primarily on polymer characteristics such as melting point, melt stability, and solubility in different solvents. The fiber formation step is accomplished by the extrusion of polymer in liquid form through fine orifices called spinnerets. The manner in which the polymer is liquefied determines the manner in which the extruded filaments are solidified. Figure 6-1 shows a simplified pictorial representation of man-made fiber manufacturing operations, excluding the polymerization reaction.

In keeping with its name, melt spinning begins with molten polymer. This process is used for polymers which can be melted under reasonable conditions without degradation, such as nylon, polyester, and olefin filaments.

Most melt spinning is integrated with polymerization units that supply the spinning operation with molten polymer. The molten polymer is metered through accurately machined gear pumps to filter assemblies consisting of either a series of metal gauzes or layers of graded sand. The filtered polymer is then extruded under high pressure and at a constant rate through a nickel or stainless steel spinneret. The extruded liquid polymer streams are cooled using an air stream and the solid filaments thus formed converge at a guide to yield spun yarn. For fibers such as nylon 6,6, the filaments pass through a steam conditioning tube before converging.

Wet solution spinning is used to produce filaments from polymer by extrusion into a liquid coagulation bath. This production method is usually reserved for the manufacture of heavy tow, which requires slower spinning and processing speeds than in melt or dry spinning. This method is used primarily to produce acrylic and modacrylic tow.

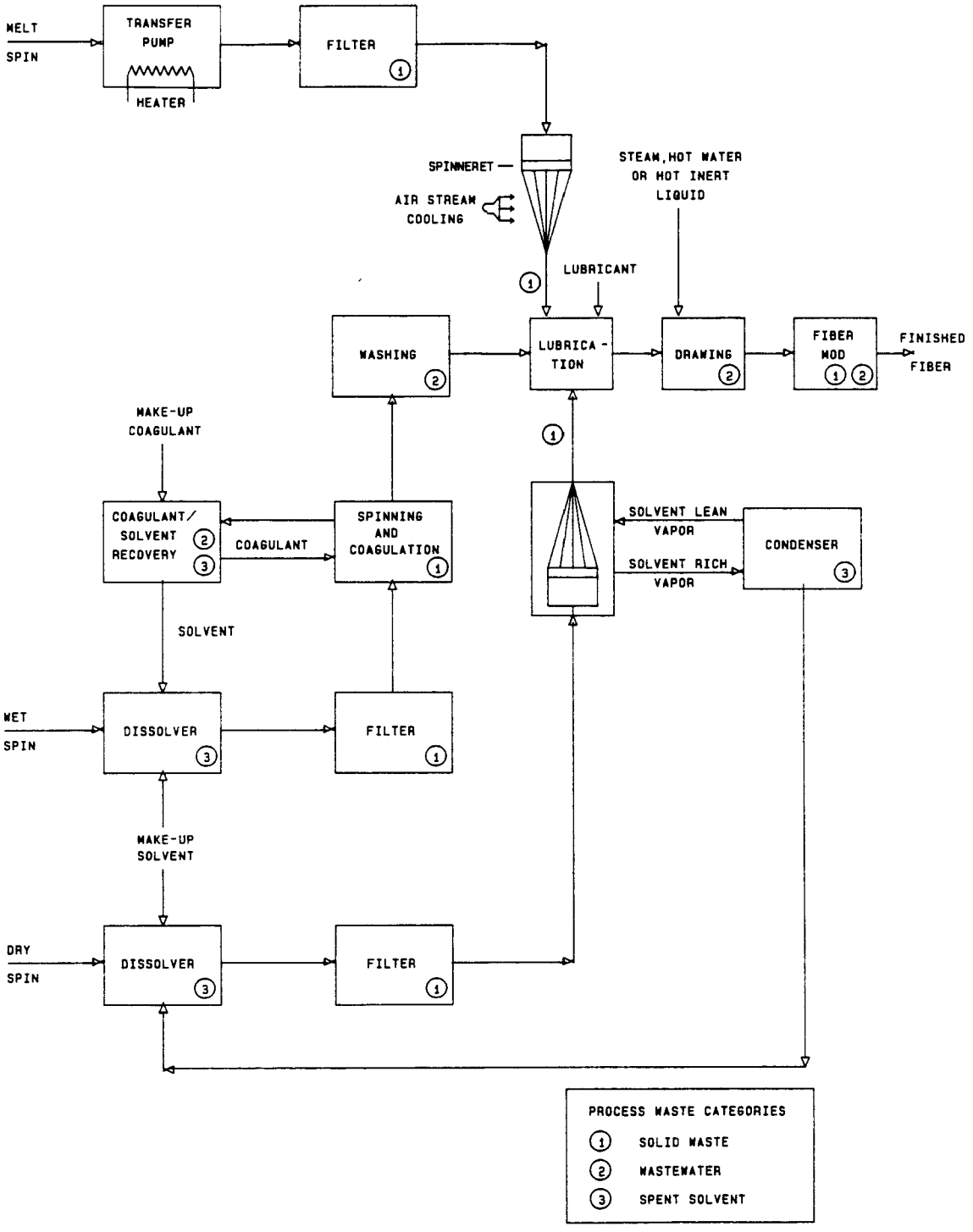

Figure 6-1 Synthetic Fiber Manufacturing Block Flow Diagram

Equipment required for wet spinning includes a solution vessel, a metering pump, a filter, a spinneret, and a coagulant tank. Aging of the polymer solution (a mixture of polymer and organic or inorganic solvent) before spinning requires a holding tank. All wet spinning processes include a washing step immediately after extrusion to remove solvent and other impurities, and a recovery system to separate the coagulant and solvent. Four specific methods of wet solution spinning have been described in the literature (Monorieff 1975). As an example, one of the four methods presented by Monorieff is listed below:

- An 18 percent solution of polymer in dimethylacetamide is spun into a mixture of 2 parts dimethylacetamide and 1 part water; as the yarn emerges from the bath it is washed with water, which flows counter-currently into the spinning bath at such a rate that the bath composition is kept constant; dimethylacetamide is continually being added by the polymer as it is extruded; water is being added from the wash.

Dry solution spinning is the third process for converting polymer into filament. Polymer is dissolved in solvent and the polymer solution is then extruded into a zone of heated gas or vapor. The volatile solvent readily evaporates, leaving a solidifed filament which is then further processed. This process is used for easily dissolved polymers such as acrylonitrile, polyvinyl chloride, or polyurethane.

Gear pumps, filter packs, and spinnerets are used in much the same fashion as they are in melt spinning. After leaving the spinneret, the solution passes through a spinning cell which consists of a cabinet about 25 feet long. Hot, solvent-lean, gas or vapor enters at one end and solvent-rich gas or vapor emerges from the other. An efficient solvent recovery system is required.

The three basic finishing steps after fiber spinning are lubrication, drawing, and fiber modification. The application of a lubricant immediately after filament formation improves subsequent handling and processing. The three main functions of lubrication are surface lubrication, plasticizing action, and static protection. Lubricants are generally aqueous solutions, emulsions, or organic liquids. From a holding tank, lubricant is circulated into feeding traps where it wets ceramic wheel applicators that coat the fiber surfaces.

Drawing introduces molecular orientation to the fiber (this causes crystalization and increases density), thus producing a stronger fiber. Fibers are drawn by stretching between pairs of rolls, with the second set moving faster than the first in order to collect the drawn fiber. Drawn lengths are from 2-7 times spun length. Many fibers are drawn as an integral part of the spinning process. The drawing process may be aided by heating the fibers either through direct metal-to-fiber contact, by passing the fibers through a bath containing a heated liquid, or by passing the fibers through a steam jet. In some cases, drawing may be combined with other processes such as cleaning or lubrication.

The function of the fiber modification step is to add attributes necessary for a marketable product. Modifications include twisting to produce interfilament cohesion, heat setting or heat relaxation to produce dimensional stability, crimping to add bulk and resilience, or cutting to produce staple products similar to natural fibers. Other processing steps sometimes utilized are treating with water-repellant, fire retardant, or other finishes.

7. WASTE DESCRIPTION

The primary specific wastes associated with the manufacturing of synthetic fibers are listed in Table 7-1. Relatively little data was available on the environmental impact of the man-made fibers industry (Farr 1977). The same remains true today. The polymer materials are not toxic or otherwise hazardous unless heated to temperatures at which decomposition can occur. Wastes from the fiber industry usually arise from mechanical treatment of the polymer or are associated with auxiliary materials used in processing such as solvents, additives, lubricants, or finishes. Companies which use integrated polymerization spinning systems also produce waste which contains unreacted monomer.

Most of the solid waste is waste fiber that is generated during startup of the process or during times of upset. This waste fiber can be generated at the spinning, drawing, and fiber modification steps. In the past, much of this waste was incinerated or landfilled. Currently, much of this waste is reprocessed either on-site (converted back into polymer and respun) or off-site (production of plastic bottles, for example). When waste fiber contains highly degraded polymer or has become heavily contaminated with machine oil or dirt, then it is incinerated or landfilled.

Table 7-1 Synthetic Fibers Manufacturing Process Wastes

No.	Waste Description	Process Origin	Composition	RCRA Codes
1.	Solid wastes	Filtration; pump seals; waste fiber; incineration residue	Polymer, filter sand; fiber finishers; TiO_2; others	--
2.	Solvent vapor	Evaporation from fiber; scrubber loss	Solvents (see Section 5)	--
3.	Contaminated solvent	Solvent purification and recovery	Solvents (see Section 5)	--
4.	Contaminated coagulant bath	Wet spinning	Water; glycerol; $CaCl_2$; dimethylacetamide; others	--
5.	Contaminated drawing bath	Wet drawing	Water; glycerol; $CaCl_2$; dimethylacetamide; others	--
6.	Polymerization by-products	Nylon 6,6 polymerization, polyester from TPA	Contaminated water	--
7.	Wastewater	Coagulant bath treatment; polymerization by-product	Contaminated water	--
8.	Spills/leaks	Undefined	Water	--
9.	Air emissions	Scrubber; steam jets; tank breathers; evaporation from fiber	Mostly solvent and incineration products	--

Wastewater is generated whenever the level of contaminants in the inorganic coagulant, washing, or drawing batch becomes an unacceptable and purging is required. Usually, drawing bath purges can be treated and used as make-up to the washing bath. In addition, washing bath purges can also be treated and used as make-up to the coagulant bath provided a water-based coagulant is being used. Many of the impurities (solvent carried into the washing bath by the fiber, for example) can be recovered during treatment and be recycled to the appropriate operation. When the need for water in a previous step does not exist, the wastewater can be used to formulate finishes. Since the fiber absorbs some water during processing, there is usually a constant demand for water in the finishing operation. Only the purging of the inorganic coagulant bath produces a major wastewater steam that requires treatment and subsequent disposal.

Wastewater ia also generated as a by-product of certain polymerization reactions. With the production of nylon or the polymerization of acrylonitrile, most of the water produced is used elsewhere in the facility. With polyester, the by-products depend on the starting monomer. If terephtalic acid is used, the by-products are water and glycol. If dimethyl terephthalate is used, the by-products are methanol and glycol. Glycol is recycled within the polymerization process while methanol is usually sold for reprocessing back into DMT or used as fuel.

Fiber manufacturers try to limit the escape of organic solvent from their processes to the fullest degree practical because of economic, safety and regulatory compliance considerations. For this reason, most solvent losses are either accidental or occur at very low levels of concentration (scrubber exhausts), where further recovery becomes unfeasible. Bottoms from the solvent recovery operation used in wet spinning is usually incinerated. When inorganic solvents are used, the contaminated solvent is discharged to the facilities wastewater treatment system.

8. WASTE GENERATION RATES

As stated earlier, very little data was available on specific waste generation rates from synthetic fiber production facilities. Waste stream information was given mainly in the form of general comments related to production of a particular fiber. It appears that aqueous emissions from wet spinning processes (coagulation bath purges) represent the largest potential source of emissions. Next, is by-product water from polymerization.

To a great extent, purge rates from coagulation baths depend on the type of bath and the age of the manufacturing plant. Glycol baths are less likely to be discarded than calcium chloride baths, due to the greater value of the glycol. The age of the plant comes into play because early designs did not incorporate features for reusing coagulation baths to the extent that those features would be incorporated today.

By-product water from polymerization, by its nature, must contain organic contaminants. These contaminants would conist of the monomers used in producing the polymer. Table 8-1 gives wastewater generation rates for nylon 6,6 and polyester from TPA. The values are based on the stoichiometry of the chemical reactions. A fair amount of this water is used where water containing small quantities of organic matter is not objectionable (n some finishes, for example).

Table 8-1 Stoichiometric By-Product Water

Fiber	By-Product Water (gal/10^3 lbs fiber)
Nylon 6,6	9.5
Polyester from TPA	22.7

Wastewater emissions from some operations have been classified according to waste load and treatability (Farr 1977). This information is summarized in Table 8-2. Analysis of samples from a settling pond at an acrylic fiber production facility indicated the presence of acrylonitrile (100 mg/l), 2,3-dibromo-1-propanol (0.5 mgl/l), an isomer of dibromopropene, and 2,4-dimethyl-diphenylsulfone.

Table 8-2 Summary of Wastewater Data for Selected Fibers

	Wastewater	Raw Waste Loads (lb 10^3 product)		
Fiber	(gal/10^3 lb fiber)	BOD	COD	Suspended Solids
Nylon	0.16-3.71	0.1-60	0.2-90	0.1-6.0
Olefin (polypropylene)	1.00-1.71	0.4-1.1	1.8-2.6	0.2-2.2

Source: Industrial Process Profiles for Environmental Use (Farr 1977).

Overall current waste generation rates for the fiber manufacturing industry were not in evidence at the time of final document preparation. Fractional waste generation (the fraction each waste represents of the total waste generated) was estimated by the project staff based on the available data and engineering judgement. These values are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

A summary of the waste sources and the corresponding source reduction methods is given in Table 9-1. This section deals with the description of the listed methods, including known application cases.

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" has also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- Waste stream segregation
- Personnel practices
  - management initiatives
  - employee training
- Procedural measures
  - documentation
  - material handling and storage
  - material tracking and inventory control
  - scheduling
- Loss prevention practices
  - spill prevention
  - preventive maintenance
  - emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Solid Wastes

Fiber spinning operations generate solid wastes including filter residues and waste fibers. The filter residue wastes are generally minor compared to waste fiber. Waste fiber comes mostly from process upsets or during spinning machine startups. Mechanical fiber modification operations, such as twisting, crimping, or cutting, also produce solid waste in the form of particulates and waste fiber. Several methods for waste reduction through source control were noted:

- Recycle waste fiber.

  Waste fiber that does not contain surface finish materials is relatively easy to reprocess. In the case of polyester, it can be sold to a PET (polyethylene terephthalate) bottle reprocessor. In the case of all thermoplastics, this fiber can be remelted and respun, but a loss of quality generally results due to thermal degradation. At least one company markets a processor for chopping up thermoplastic waste and pelletizing it. Clean acrylic waste is easily redissolved and respun; the economics of this are so clearly in favor of it, in fact, that it is widely practiced.

  Waste fiber containing surface finishes is often reprocessed by washing the fiber in detergents, chopping the wet fiber, and flash drying it. In those cases where waste fiber cannot be recycled due to surface contamination, the causes for surface contamination should be identified and eliminated.

- Increased automation

  The revolution now underway in electronics has spawned a new generation of instruments such as tenacity gauges, optical inspection devices, differential thermal analysers, etc. that can be employed to catch process upsets at an early stage.

- Good operating practices

  Good operating practices include determination of the causes for process upsets and their subsequent minimization, examination of start up procedures, identification of devices and methods that will cut waste production, and commitment to an effort to develop additional methods of

salvaging off-grade fiber. An accounting system (or checklist) for identifying origins of waste fiber appears worthy of consideration.

9.1.2 Wastewater

Fiber spinning also results in the generation of liquid wastes, primarily from wet spinning. A large portion of liquid waste occurs when the coagulation bath is entrained on fiber surfaces into subsequent wash stages. Liquid wastes are also generated in the drawing and chemical fiber modification operations and during the polymerization reaction of the polymer. For ways in which aqueous wastes associated with equipment cleaning can be minimized, the reader is referred to the study on equipment cleaning contained in this appendix. Methods for minimizing aqueous waste include:

- Redesign of washers.
  The greatest potential for improved water economy stems from the use of better washing methods (Masselli 1973). Washers should be designed to use only the amount of water necessary for a particular step or operation. Rodney-Hunt, manufacturers of the tersitrol washer, compared their washer to two tight-strand washers and suggested that up to 85 percent less water use may be achievable (USEPA 1974).

- Use multistage counter-current wash system.
  By using a multistage counter-current wash system, a large reduction in the amount of water required for washing can be achieved. Since the system produces a much more concentrated effluent stream, it is often practical to concentrate the stream (by means of evaporation) and recycle the material. In the wet spinning process, coagulant is entrained on the fiber and carried over into subsequent wash baths. By producting a wash water wastestream as concentrated as possible, the feasibility of recycling this waste back to the coagulation bath can be improved.

- Use oil and lubricant substitutes.
  Carding oils and antistatic lubricants can be replaced by mineral oils with nonionic emulsifiers and other low-BOD substitutes (Masselli and Burford 1956). This change improves the treatability of the lubricant waste generated. In addition, this method improves the treatability of the

In dry spinning, the recycled solvent does not build up objectionable impurities so that it can be reused indefinitely. Solvent losses occur almost exclusively through evaporation. These losses can be minimized by reducing the leakage of non-condensibles during spinning.

In wet spinning, contaminated solvent becomes a problem only in isolated cases. Usually, the preferred method for dealing with this material is to sell it back to the solvent supplier or to install on-site distillation equipment.

9.2 Implementation Profile

Reduction of the waste load generated by fiber manufacturers can be accomplished to a large extent through the employment of modern instruments and equipment, advanced processing techniques, and careful identification of the origins of waste. Water usage control techniques have been extensively studied and documented; manufacturers of synthetic fibers are expected to have applied these to a high degree methods to reduce their wastewater load. Additional waste reduction will come from improvements in operating practices -these are the easiest to apply.

9.3 Summary

A summary of the source reduction techniques along with the associated ratings is given in Table 9-1. The ratings represent the assessment of the relative usefulness of the proposed techniques. Each method is rated on an integral scale of 0 to 4 with respect to its waste reduction effectiveness, extent of current use, and future application potential. Based on these ratings, current and future waste reduction indices are derived to provide a measure of current and future extent of waste reduction for each technique, each waste stream, and the entire process.

A current reduction index (CRI) of 2.3 (58 percent) is indicative of the high level of waste reductions achieved by the synthetic fibers industry. CRI represents the ratio of the amount of waste that was reduced to the amount that would be generated if none of the measures listed were used at their current level of application. By implementing additional source reduction techniques, the amount of waste currently being generated can be reduced to a modest extent, as evidenced by a future reduction index of 0.5 to 0.8 (13 to 20 percent). As seen from Table 9-1, the most effective

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE SYNTHETIC FIBERS MANUFACTURING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Solid Wastes	1. Recycle waste fiber	2	2	2	3	1		1.5	0.1	
	2. Increased automation	1	1	3	2	3		1.5	1.1	1 1
	3 Better operating practices	1	1	3	3	3		2.3	0.6	
	Overall	1.33	1 33	2 67	2 67	2.33	0.10	2.3	0 6	1.1
Wastewater	1. Redesign of washers	2	1	2	1	2		0.5	0 8	0 8
	2. Use counter-current wash system	2	1	3	2	2		1 5	0 8	0 8
	3. Use oil and lubricant substitutes	1	1	1	2	1		0.5	0 1	
	4 Fractionate by-product water	0	0	1	1	1		0 3	0 2	
	5. Increased automation	1	1	2	2	2		1 0	0.5	
	6. Better operating practices	1	1	3	3	3		2.3	0.6	
	Overall	1 17	0.83	2.00	1.83	1 83	0.85	2.3	0.5	0.8
Contaminated Solvent (*)	1. Maintain solvent recovery / recycling	1	1	4	3	1		3.0	0.3	0 3
	Overall	1.00	1.00	4.00	3.00	1 00	0.05	3.0	0 3	0 3
All Sources	All Methods						1.00	2.3	0 5	0.8

(*) These streams include listed "F" and/or "K" RCRA wastes

measures that can be used to achieve this reduction include better water usage e.g. through redesign of washers, use of multistage counter-current washing, increased automation, and implementation of better operating practices. Current measures that have been very effective include recycling of waste fiber, recycling of solvent, and good operating procedures.

10. PRODUCT SUBSTITUTION ALTERNATIVES

From the earliest days of rayon, the demand for man-made fibers has continually increased. Combined production of polyester, nylon, and acrylic fibers was up about 14% from 1982 to 1983 (Greek 1983). This is a clear indication that man-made fibers will continue to increase in demand.

No viable alternatives to man-made fibers have been identified; that is to say, man-made fibers possess certain physical properties (e.g. wear and wrinkle resistance) which have enabled them to compete effectively with certain natural fibers such as cotton and wool. Presently, it would be unrealistic to assume that this trend will ever reverse.

11. CONCLUSIONS

Generally, very little documentation was found concerning the extent to which fiber producers have implemented waste reduction measures. Estimates indicate that solvent recovery, waste reprocessing, and wastewater reductions are practiced widely for economic reasons. It should be noted that each individual fiber production facility may have its own specific production and finishing steps. Therefore, the extent of reduction possible in one facility may differ greatly from that in another facility. For the synthetic fiber industry, it is estimated that modest future reduction in waste volumes are possible. The largest reductions in waste will center on ways of decreasing wash water use. The industry has done much in the area of reducing solid and solvent waste by recycling these materials.

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13. INDUSTRY CONTACTS

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1. PROCESS: SYNTHETIC RUBBER MANUFACTURE
2. SIC CODE: 2822
3. INDUSTRY DESCRIPTION

The industry consists of establishments primarily engaged in manufacturing synthetic rubber by polymerization or copolymerization of monomeric feedstock. An elastomer, for the purpose of this classification, is a rubber material capable of vulcanization, such as copolymers of butadiene and styrene, or butadiene and acrylonitrile, polybutadiene, chloroprene rubbers, and isobutylene-isoprene copolymers. Butadiene copolymers containing less than 50 percent butadiene are classified in SIC 2821. Natural chlorinated rubbers and cyclized rubbers are considered as semi-finished products and are classified in SIC 3069.

3.1 Company Size Distribution

The synthetic rubber industry consists of five major producers accounting for about 75 percent of the total production in the United States. More than 55 percent of the 77 synthetic rubber plants employ less than 20 employees each. Table 3-1 shows the company size distribution of the synthetic rubber industry for 1982.

Table 3-1 Company Size Distribution

	No. of employees per facility					
	Total	1-19	20-49	50-99	100-999	1000+
No. of establishments	77	43	4	6	22	2
No of employees	11,800	200	600	no data	11,000	no data

Source: 1982 Census of Manufacturers (USDC 1985).

3.2 Principal Producers

Table 3-2 lists the major producers of synthetic rubber along with their annual capacity. The types of rubber considered are styrene-butadiene rubber (SBR), polybutadiene rubber (PBR), neoprene or chloroprene rubber (CR), ethylene-propylene

Table 3-2 Principal Producers of Synthetic Rubber

Company and Plant Location	Annual Capacity (Thousands of Tons)						
	SBR	PBR	CR	EPR	IIR	IR	NBR
American Synthetic Rubber Co.							
Louisville, KY	70	50					
Cities Service Co., Inc.							
Lake Charles, LA					38		
Copolymer Rubber & Chemical Co.							
Baton Rouge, LA	125						5
Addis, LA				33			
Denka Chemical Co.							
Houston, TX			27				
E.I. du Pont de Nemours Co.							
Laplace, LA			36				
Louisville, KY			134				
Beaumont, TX				77			
Exxon Co.							
Baton Rouge, LA				60	85		
Bayton, TX					105		
The Firestone Tires Rubber Co.							
Pottstown, PA	3						
Akron, OH	50						
Lake Charles, LA	310						
Orange, TX	45	110					
The B.F. Goodrich Co.							
Orange, TX		74	22			65(a)	
Port Noches, TX	152						
Akron, OH							14
Louisville, KY							28
The General Tire & Rubber Co.							
Borger, TX	40						
Mogadore, OH	15						
Odessa, TX	83						
The Goodyear Tire & Rubber Co.							
Calhoun, GA	7						
Houston, TX	395						16
Beaumont, TX		115				60	
Akron, OH						3	
Philips Petroleum Co.							
Borger, TX	96	68					
Polysar Resins, Inc.							
Chattanooga, TN	30						
Texas - U.S. Chemical Co.							
Port Noches, TX	183						
U.S. Steel Co.							
Scotts Bluff, LA	15						
Uniroyal, Inc.							
Geismar, LA				44			
Paineville, OH							16
Total	1,624	420	197	236	228	125	82

Source: Chemical Economics Handbook (SRI 1980).
(a) Plant not operating at present.

rubber (EPR), butyl or isobutylene-isoprene rubber (IIR), polyisoprene or isoprene rubber (IR), and nitrile or acrylonitrile-butadiene rubber (NBR).

3.3 Geographical Distribution

Since most synthetic rubber is used for tires and tire products, the industry is concentrated near automobile assembly plants in Michigan or close to raw material sources in Texas. There are twelve establishments in Texas, six each in Michigan and Louisiana, and four each in New York, New Jersey and Ohio. The location of establishments in the U.S. is shown in Figure 3-1 and Table 3-3 below.

Table 3-3 Location of Facilities by EPA Region

EPA Region	Number of Establishments
I	--
II	8
III	1
IV	8
V	10
VI	18
VII	--
VIII	--
IX	--
National	77

Source: 1982 Census of Manufacturers (USDC 1985).

4. PRODUCTS

In 1977, it was estimated that about 65 percent of the synthetic rubber produced was used for tires and tire products (Parr, Parson, and Phillips 1977). The annual production rates for some significant types of rubber are listed in Table 4-1. Table 4-2 shows the use pattern of these same types of rubber.

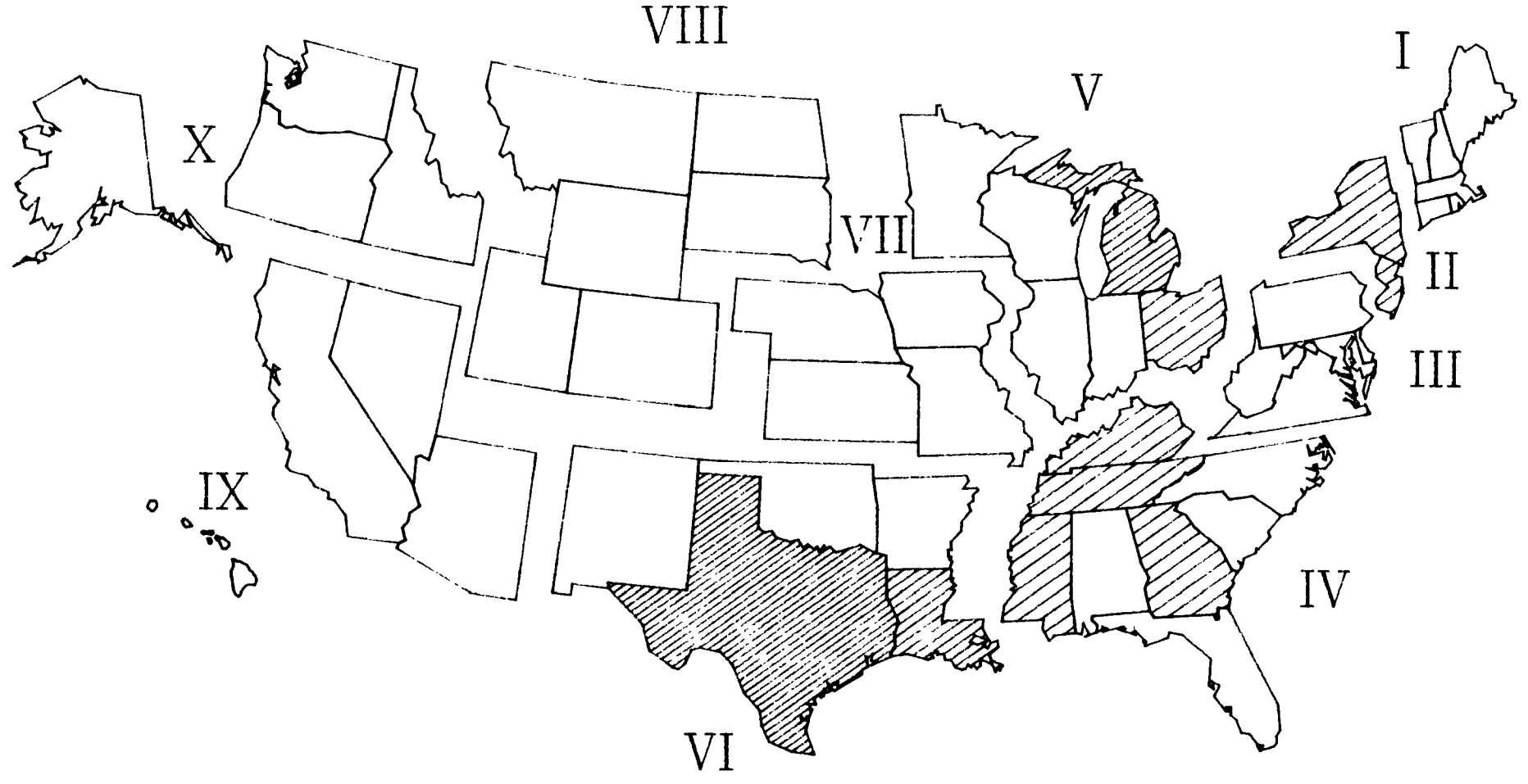

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Figure 3-1 Synthetic Rubber Plants in the U.S.

Table 4-1 Annual Production Rates (TPY) of Various Synthetic Rubbers

Type	Abbreviation	Production TPY	Year
Styrene-Butadiene	SBR	1,420,000	1978
Rubber		958,000	1984
Polybutadiene	PBR	378,000	1978
Rubber		359,000	1984
Neoprene/Polychloroprene	CR	109,900	1975
Rubber		130,000	1984
Ethylene-Propylene	EPR	187,400	1983
Rubber		215,000	1984
Butyl Rubber	IIR	142,000	1979
Nitrile Rubber	NBR	76,000	1979
		67,000	1984

Source: Chemical Economics Handbook (SRI 1980), Chemical and Engineering News (Stimson 1985).

Table 4-2 Use Pattern of Various Synthetic Rubbers

Application	Percent Consumption						
	SBR	PBR	CR	EPR	IIR	IR	NBR
Tires and tire products	63	84	--	9	75	55	--
Automotive application	7	--	28	34	--	--	--
Mechanical goods	18	5	35	3	--	13	--
Latex applications	10	--	--	--	--	--	10
Seals and gaskets	--	--	--	3	10	3	25
Hoses	--	--	--	6	--	5	25
Footwear	--	--	--	1	--	10	5
Wire and cable insulation	--	--	13	7	--	--	--
Impact modifier	--	11	--	13	--	--	--
Others	2	--	24	24	15	14	35
Total	100	100	100	100	100	100	100

Source: Chemical Economics Handbook (SRI 1980).

5. RAW MATERIALS

Monomers	Styrene, butadiene, chloroprene, isobutylene, isoprene, acrylonitrile, ethylene, propylene, 1,5-cyclo octadiene, dimethyl siloxane, diisocyanates, ethylene glycols, ethylidene norborene, 1,4-hexadiene, dicyclopentadiene, methylene norborene, etc.
Initiators	Potassium peroxy disulfate, benzoyl peroxide, azobis isobutyronitrile, cumene hydroperoxide, p-menthane hydroperoxide, butyl lithium, nitrogen hepta sulfurimide, formamidine sulfinic acid, potassium persulfate.
Chain transfer agents	N-dodecyl mercaptan, tert-dodecyl mercaptan, thiuranes, xylene solution of tetraethyl thiuram disulfide.
Emulsifiers	Aqueous solutions of sodium stearate, sodium rosinate, disodium salt of ethylene diamine tetracetic acid, zinc stearate, sodium formaldehyde sulfoxylate.
Terminators	Sodium dimethyl dithio-carbamate, sodium nitrite, sodium polysulfide, hydroquinone.
Solvents	N-hexane, pentane, heptane, methyl chloride, naphtha, cyclohexane, benzene, toluene, xylene, chlorobenzene, propylene.
Catalysts	Butyl lithium, vanadium tetrachloride, vanadium oxytrichloride, diethyl aluminum chloride, diisobutyl aluminum chloride, ethyl aluminum sesquichloride, triethyl or triisobutyl aluminum, $TiCl_4$, TiI_4, $CoCl_2$, $AlCl_3$, BF_3.

Activators	Ferrous sulfate heptahydrate, disodium salt of ethylene diamine tetracetic acid, sodium formaldehyde sulfoxylate, zinc stearate.
Fillers	Carbon black, sulfur, aromatic (staining) oils, naphthenic (nonstaining) oils, paraffin wax, clay, whiting, titanium dioxide, silica, hydrated alumina, polyvinyl chloride.
Curing agents	Tetramethyl thiuram disulfide, mercaptobenzothiozole, zinc dibutyl diltuis carbamate, ferric dimethyl dithyio carbamate, sulfur, dicumyl peroxide, zinc oxide, calcined magnesia, etc.
Reagents	Potassium chloride, potassium hydroxide, brine, sulfuric acid, chlorine.

6. PROCESS DESCRIPTION

Synthetic rubber is manufactured mostly by emulsion polymerization, solution polymerizations, or slurry polymerization. Table 6-1 lists some synthetic rubbers and their corresponding monomers along with the polymerization schemes used. Butyl rubbers are produced by a slurry process which is considered to be similar to the solution polymerization process from a waste generation standpoint. For this reason, the slurry process is not considered separately in this study. The following sections deal with the emulsion and solution polymerization processes.

6.1 Emulsion Polymerization Process

In 1979, the emulsion polymerization process was used to produce 90% of the styrene-butadiene rubber and almost all nitrile and neoprene rubber. Since styrene-butadiene rubber accounts for more than 60 percent of all synthetic rubber produced in the U.S., emulsion polymerization is the most widely used method.

In emulsion polymerization, the monomers are emulsified in a medium, such as water, along with emulsifying agents such as soaps and synthetic emulsifiers. The

Table 6-1 Production Methods for Various Synthetic Rubbers

Rubber	Monomers	Polymerization Scheme	Temperature (°F)	Percent Conversion	Product Composition	Residence Time	Pressure (atm)
SBR	Styrene, butadiene	Emulsion (90%) Solution (10%)	112 or 41 112	60-75 98	23% styrene	8-15 hrs	4-5 1-2
PBR	Butadiene	Solution	--	70-90	98% cis	--	--
CR	Chloroprene	Emulsion	104	91	--	--	--
EPR	Ethylene, propylene, and dienes	Solution	95	--	40-50% Ethylene 3-9% diene	--	--
IIR	Isobutylene, Isoprene	Slurry	148	70-95	--	30-60 min.	2-4
IR	Isoprene	Solution	4	--	98% cis	--	--
NBR	Acrylonitrile, butadiene	Emulsion	112 or 41	75-90	30-40% Acrylonitrile	5-12 hrs	8-9

Source: Kirk-Othmer Encyclopedia of Chemical Technology (McGrath et. al. 1979) and Assessment of Industrial Hazardous Waste Practices: Rubber and Plastics Industry (Kushnir and Nagy 1978).

polymerization reaction is started by the addition of a water soluble initiator, and can be stopped at a desirable point by the addition of chemicals called shortstops (or terminators).

The first step in emulsion polymerization, as shown in Figure 6-1, is the removal of inhibitors. Inhibitors are added to some monomers to prevent premature polymerization during transport and storage. This removal is achieved by washing the monomer with a caustic solution. The caustic solution is usually recycled to the washing process until it becomes saturated with inhibitors and is then transferred to settling pits where it is mixed with other process effluents. The settling pits are used to remove suspended solids present in some effluent streams. After sufficient settling time, this stream is further treated to reduce its biological oxygen demand (BOD).

The uninhibited monomers are fed to a polymerization reactor containing water and emulsifying agents. Typical reactors have sizes varying from 5,000 to 30,000 gallons. The emulsion is created by agitators or by recirculating the mixture through centrifugal pumps, as in the case of neoprene rubber production. Initiators, catalysts, activators, and stabilizers are added to the reactor to start the polymerization reaction. The polymerization reaction is highly exothermic and proper temperature control is achieved by heating/cooling coils through which a heat transfer fluid is circulated. Additional cooling is achieved by condensing the vapors emitted from the reactor and returning the condensate to the reactor.

Polymerization is stopped at the desired degree of conversion by the addition of chemicals, called short stops, in aqueous solution. The polymerized monomer of latex is then sent to a vacuum flash unit where light monomer, along with water vapor, is separated out as overhead. This vapor stream is condensed and the light monomer is recovered by decantation to be recycled to the polymerization process. The water stream generated is sent to wastewater treatment. The noncondensible impurities are sent to a flare.

Unreacted heavy monomer present in the latex from the vacuum flash unit is removed by steam stripping the latex. Again, the vapor stream from the stripper is condensed to remove the heavy monomer by decantation, which is recycled to the process. Another aqueous waste stream is generated in this separation step.

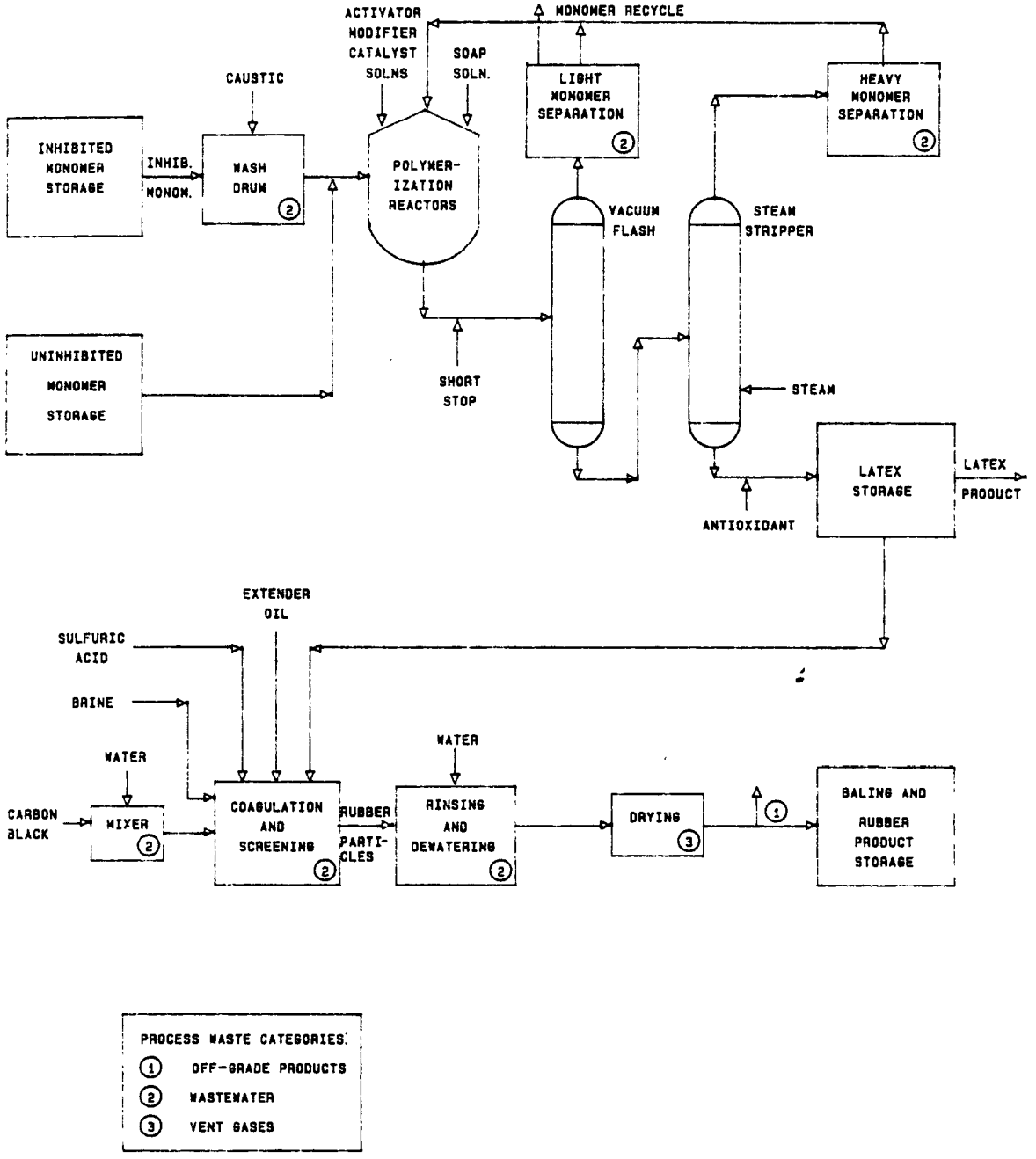

Figure 6-1 Emulsion Polymerization Process for Synthetic Rubber Manufacture

The latex, thus freed of monomers, is mixed with antioxidants and sent to latex storage, where it can be sold as a product. When the product is to be sold as bales, the rubber particles dispersed in the latex need to be solidified. This is done by coagulating the rubber particles, which causes them to settle faster due to their increased size. To achieve this separation, the latex is sent to a coagulation tank where it is mixed with brine. The brine causes the latex to "cream," which is a partial flocculation of the rubber particles. This flocculation is caused by the breaking of the emulsion, resulting from the altered ionic interaction between emulsion components. The emulsifiers are thus separated from the rubber particles, though the particle size of the rubber is still too small for rapid settling. Addition of dilute sulfuric acid causes these particles to agglomerate. Sometimes extender oils in aqueous emulsion and carbon black in slurry form are added to the latex prior to coagulation. The particles from the coagulation liquid are separated on a shaker screen. The liquor is recycled with fresh brine and acid make-up. The liquor overflow (blowdown) is a significant waste stream and is sent to settling ponds before being sent to waste treatment. The screened rubber particles from the coagulation tank are slurried in water and sent for further processing.

The screened rubber particles slurried in water are rinsed with more water and are then filtered and dewatered in rotary vacuum filters. The filtrate is sent to a reslurry tank where some of the liquid is discharged to waste treatment and the remainder is recycled to the rinsing unit. The dewatered crumbs are dried using hot air in continuous or screen dryers. The dry product is weighed and formed into bales using hydraulic balers and sent to product storage.

6.2 Solution Polymerization Process

Solution polymerization is the other major process for synthetic rubber manufacture, used mostly for the production of polybutadiene, polyisoprene, ethylene-propylene rubbers, and part of styrene-butadiene rubbers. The use of solution polymerization for SBR (the major synthetic rubber produced), is expected to grow because SBR made by solution polymerization has better rolling resistance and other desirable qualities (McNaughton 1983).

In solution polymerization, the monomers are dissolved in a solvent, such as an aromatic, aliphatic, or alicyclic hydrocarbon. Addition of catalysts of the Zeigler-

Natta or Friedel-Crafts type starts the polymerization reaction. As the polymer forms, it precipitates out since it is insoluble in the solvent. The reaction can be stopped at any time by the addition of shortstops.

The solution polymerization process is shown schematically in Figure 6-2. The removal of any inhibitor present in the monomer is achieved in a manner similar to that used in the emulsion polymerization process. The uninhibited monomers are then mixed with the solvent and the mixture is dried in a desiccant column. The solid desiccant used for drying is regenerated or discarded. The regeneration step may produce some aqueous waste and the discarded desiccant is a solid waste.

The dried monomer is sent to the polymerization reactor where a catalyst, which can be a complex alkyl of metals such as titanium or aluminum, is added to start the polymerization. The reaction produces heat, which is removed by cooling coils in which a suitable refrigerant is circulated. The reaction is terminated at the desired point by the addition of shortstops.

The polymer slurry from the reactor is then treated with liquids such as aqueous alcohol. The alcohol allows the transfer of the catalyst to the aqueous phase, leaving the now catalyst-free polymer slurried in the solvent. The aqueous alcohol/catalyst solution is treated to precipitate the catalyst as metallic oxides, and recover solvent and alcohol to be recycled to the process. The metal oxides, suspended in water, are mixed with other effluents and sent to waste treatment. The polymer slurry is mixed with antioxidants and extender oil and is stored in a suspension form called rubber cement.

The rubber cement is sometimes mixed with carbon black slurry and then contacted with hot water (for butyl rubbers) or steam (for others). This operation removes the solvent and unreacted monomers while coagulating the rubber at the same time. The vapor stream from this process is distilled to recover solvents and monomers which are recycled to the polymerization process. Distillation produces an aqueous waste stream and an organic stream containing oily slops. The aqueous stream is either sent directly to wastewater treatment or is steam-stripped before discharge. The oily wastes are used as a fuel or processed for further purification. The polymer crumb slurry thus generated is dewatered, screened, dried, and baled by processes similar to those used for producing bales in the emulsion polymerization process.

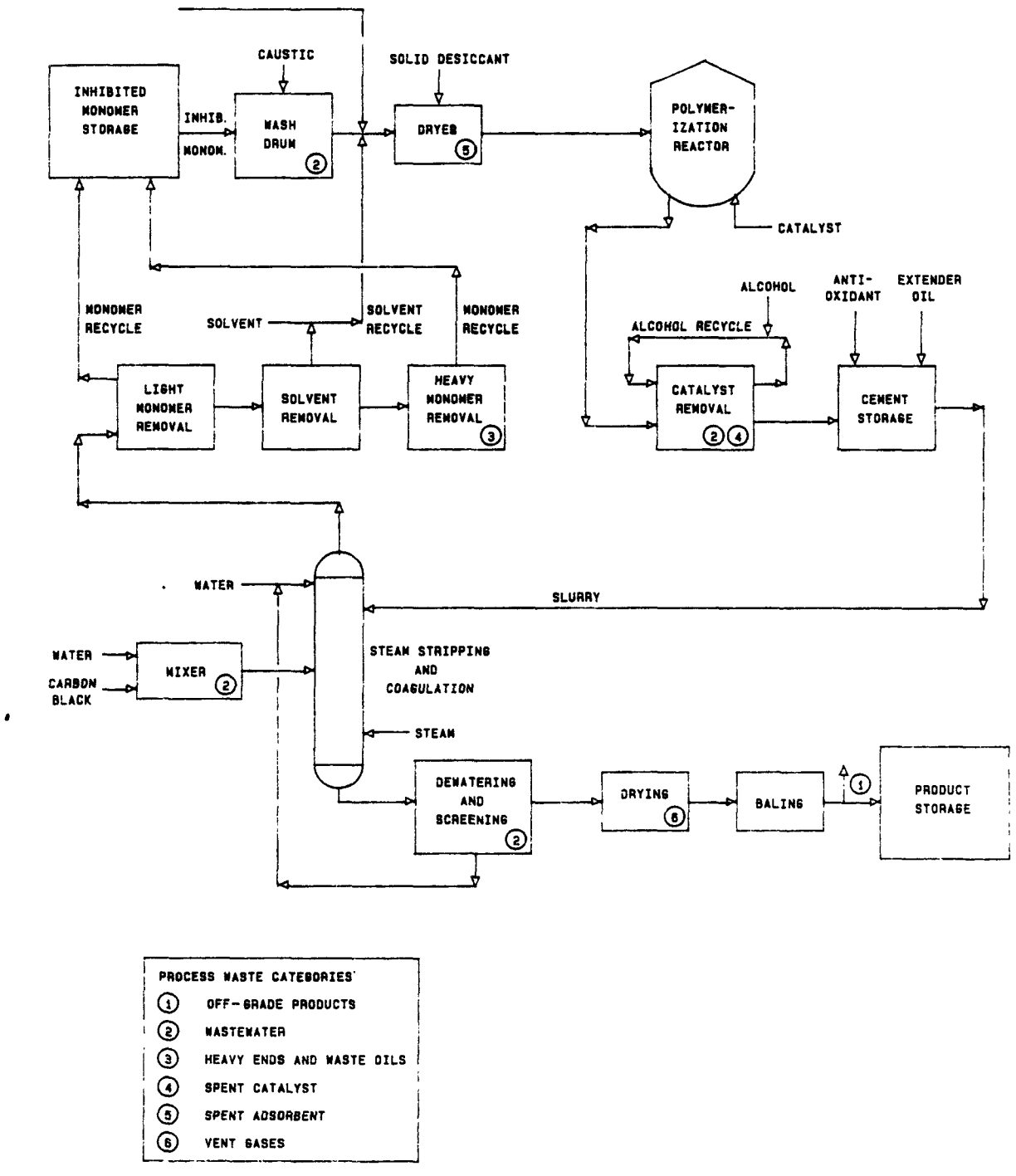

Figure 6-2 Solution Polymerization Process for Synthetic Rubber Manufacture

7. WASTE DESCRIPTION

Table 7-1 lists the primary wastes associated with synthetic rubber manufacturing both by emulsion and solution polymerization.

Off-grade products, which amount to 1 to 3 percent of total production, are the result of bad batches and product changes. This stream contains rubber particles with different degrees of contamination suspended in water (in the case of emulsion polymerization), or a solvent (in the case of solution polymerization). This stream is usually mixed with other effluents and sent to settling pits where the solid particles separate out. These solids are removed periodically and are reused, landfilled, or incinerated depending on the degree of contamination.

Periodic cleaning of the equipment results in aqueous and organic wastes. The solid particles suspended in water are usually recovered at the settling ponds, as are the heavy ends and waste oils present in the waste water. Since solution polymerization involves the use of solvents (and hence requires a water-free environment) very little water would be used for cleaning equipment used in the solution process. Solvents used for cleaning can be collected and reused in the process.

Other aqueous wastes result from inhibitor removal, monomer and solvent recovery, coagulation dewatering, rinsing, screening and carbon black slurry preparation operations. The inhibitor removal achieved by caustic wash generates an aqueous stream containing phenols. As this stream is usually reused until it is completely saturated, its discharge is intermittent. Solvent and monomer recovery operations consist of condensation, decantation, and distillation of the vapor overheads from the reactor. Since this aqueous stream contains a significant amount of dissolved organics, it is usually steam-stripped to remove the volatiles before being mixed with other effluents. Coagulation of the latex in emulsion schemes is achieved by the addition of brine and sulfuric acid solutions. The coagulation overflow is the major portion of all the aqueous wastes. Overflow from carbon black slurry preparation is an aqueous waste containing suspended carbon particles. All the above streams are mixed and sent to settling pits where the solids and oils are removed. The aqueous effluent from these pits is sent to treatment plants where the biological oxygen demand (BOD) is lowered to acceptable levels.

Table 7-1 Synthetic Rubber Manufacturing Wastes

Waste Description	Process Origin	Composition	RCRA Codes
Off-grade products	Bad batches, production changes	rubber particles containing traces of unreacted monomers, solvents, catalysts and other additives	--
Equipment cleaning wastes	Washing operations on various equipment	rubber particles in water containing organics	--
Other aqueous waste	Monomer solvent separations, rinsing, filtering, de-watering, coagulation, screening, inhibitor removal, carbon black slurry making operations	rubber particles, carbon black, and various organics in water	
Heavy ends and waste oils	Monomer and solvent recovery operations in solution polymerization, oils separated from aqueous wastes	Monomers, solvents, extender oils, etc.	--
Spent catalyst	Catalyst removed in solution polymerization	Oxides of titanium, aluminum	--
Spent adsorbent	Feed drying in solution polymerization	Traces of monomers, solvent in solid adsorbent	--
Spills	Various process equipment and piping	Monomers, solvents, oils, etc.	--
Gaseous emissions	Leaks, drying and stripping operations, adsorbent regeneration in solution polymerization	Monomers, solvents, etc.	--

Heavy ends and waste oils are generated by the solvent and monomer recovery operations, and by the entrainment of extender oils in the coagulation overflow. The heavy ends generated in the distillation operations contain significant hazardous organic materials. This stream is mixed with waste oils recovered from the settling pits and incinerated or drummed for land disposal.

Solution polymerization requires the removal of catalyst. This catalyst is usually removed by an undisclosed process in the form of metallic oxides suspended in water. This stream is expected to be small and is probably mixed with other aqueous streams and sent to settling pits, where the catalyst particles along with other suspended material settle out. The solids are periodically removed and disposed of as described previously.

The monomer and solvent dehydration operations in solution polymerization are accomplished by using solid desiccant. This adsorbent is regenerated periodically and discarded eventually as a solid waste. This waste is expected to be small and information on the disposal methods was not found.

Spills that occur in various parts of the plant due to accidental discharges generate another waste stream. This stream is usually mixed with other streams and disposed of as explained before. The gaseous waste streams are generated by fugitive emissions at various parts of the plant, air drying of rubbers, and non-condensables vented from flashing and stripping operations. The gas streams are generally vented to the atmosphere in high-level stacks or sent to a flare for incineration.

8. WASTE GENERATION RATES

Current waste generation rates were not in evidence at the time of final document preparation. Table 8-1 lists 1974 nationwide waste generation rates for various synthetic rubbers. Based on a review of the other process studies, it is likely that these rates have changed dramatically due to RCRA.

Table 8-1 1974 Nationwide 1984 U.S. Waste Generation Rates for Various Synthetic Rubbers in metric tons per year

No.	Waste Source	Emulsion SBR	Solution SBR	PBR	CR	EPR	IIR	IR
1)	Off-grade products	28,600	2,200	1,000	5,300	0(a)	0(b)	NA
2)	Equipment cleaning wastes	5,700	2,200	NA	NA	NA	NA	NA
3)	Other aqueous wastes	incl.(2)	incl.(2)	NA	NA	NA	NA	NA
4)	Heavy ends and waste oils	2,900	2,200	50	10,600	0(b)	NA	NA
5)	Spent catalyst	NA	NA	NA	NA	30	NA	NA
6)	Spent adsorbent	NA	NA	50	NA	100	100	NA
7)	Spills	incl .(4)	incl.(4)	incl .(4)	incl.(4)	incl.(4)	NA	NA
8)	Fugitive emissions	NA	NA	NA	NA	NA	NA	NA

Source: Assessment of Industrial Hazardous Waste Practices (Kushnir and Nagy 1978) and Industrial Process Profiles for Environmental Use (Parr, Parson, and Phillips 1977).

(a) Material was sold for special use.

(b) Use was found for the material at the production site.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

The list of individual waste streams and their sources along with the source reduction methods are presented in Table 9-1. In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" has also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel practices
  - management initiatives
  - employee training
- o Procedural measures
  - documentation
  - material handling and storage
  - material tracking and inventory control
  - scheduling
- o Loss prevention practices
  - spill prevention
  - preventive maintenance
  - emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Off-Grade Products

Off-grade products are the result of operator error or system malfunction. The product lost due to this waste stream amounts to 1-3 percent of the total production. This solid waste is either sold as an off-grade product or buried in landfills, depending on the degree of contamination. These solids contain traces of unreacted monomers

and other additives and may pose an environmental hazard. The following source reduction methods are noted:

- Reduction of polymer buildup on the reactor walls.
  During the polymerization reaction, the polymer that forms may build up on the reactor walls. This impairs heat transfer resulting in poor temperature control and thus contributes to lower product quality. It may even result in production of a bad batch. Preventing polymer buildup on the reactor wall can be done by spraying or rinsing the reactor walls with certain chemicals as is done with polyvinyl chloride reactors (Wilkins 1977), using Teflon* liners on the reactor walls to reduce adhesion, or installing mechanical wall wipers inside the reactor (Wilkins 1977).

  Teflon* liners are suggested because the anticipated low adhesion between Teflon and the polymeric material should reduce buildup. Tank designs employing dual shaft mixers, one serving the mixer and another one for the wiper blade, are available commercially and have been used extensively for viscous fluid mixing applications.

- Using continuous versus batch operation.
  From a waste generation standpoint, continuous operation is preferable to batch operation because it requires less equipment cleaning, and because the probability is operator error leading to production of a bad batch is lower. This is due to the higher degree of human involvement required for a batch operation. Neoprene rubber is usually made by a batch operation and its manufacture suffers from 3 percent product loss. Continuous operation for Neoprene rubber and for SBR, have been developed and can cut down both product loss and waste generation (Huisingh et. al. 1985; Aho 1958; SIR 1968). Most SBR is already produced by continuous operation. Application of a continuous process concept to Neoprene rubber can be re-examined in the context of waste generation and reduction.

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- Increased automation.

  By increasing the degree of automation, operator errors that result in bad batches could be avoided. Automation is typically simpler and less costly in a continuous process as opposed to a batch, or discrete, process.

- Backup systems.

  Emergencies, such as power failures or equipment failures, should be considered in the design or production planning stage and contingency procedures should be worked out. An interruption of cooling water flow can cause a run-away reaction which, in addition to being a safety hazard, may generate large waste quantities. By using diesel or steam turbine-driven pumps to provide cooling water during a power failure, this can be avoided. Automatic back-up power systems and chemical injection systems that spray short stops to stop polymerization are some alternatives. Such systems are used in the manufacture of polyvinyl chloride (Wilkins 1977).

- Finding use for off-grade products.

  By blending off-grade products with other rubbers or rubber wastes, a useful rubber product can be made (Zimmerman 1981; Anonymous 1982a). This is done extensively for both butyl and ethylene-propylene rubber.

  French researchers report a procedure whereby raw materials can be recovered from the off-grade products (Anonymous 1982b). The process consists of dissolving the off-grade products in an oil (primarily composed of aromatic compounds) at 572-716^{o}F. Carbon black and rubber (free of monomer) can be recovered from this solution.

  In another process, off-grade products are depolymerized in a liquid hydrocarbon medium by means of agitation, heat, free radical initiators and molecular oxygen (Scott 1972 and USEPA 1975). The rubber-modified hydrocarbon that results can be vulcanized to produce a moisture barrier or insulation coating. It can also be blended with asphalt to provide rubberized asphaltic composition, or thermally decomposed to produce carbon black.

9.1.2 Equipment Cleaning Wastes

Equipment cleaning wastes are the result of various washing operations performed on the reactors and other process equipment. The reactors in the emulsion scheme are usually washed with water, thereby generating an aqueous waste. In solution schemes, since the reactors should be kept free of water, organic solvents are used to wash the reactors. This organic stream can be treated to remove the solvent and the dissolved rubber can be precipitated to be reused or discarded as a waste. The following techniques for reducing wastes from equipment washing operations were noted:

- Reduction of polymer build-up on the reactor walls.
  Reduction of polymer build-up on the reactor walls by using Teflon* liners or spraying chemicals on the walls reduces the required equipment washing frequency and therefore results in less wastewater being produced. Use of reactors equipped with wipers that continuously clean the walls is another practical alternative.

- Altering product composition.
  Changing the product composition can reduce the concentration of contaminants in the aqueous waste. For example, SBR typically contains 23 percent styrene and the increasing cost of styrene has prompted some manufacturers to lower the styrene content to 15 percent (Anonymous 1985). This results in a lower styrene content in the waste wash water.

  By increasing the degree of polymerization allowed, rubbers with higher molecular weights could be produced. This higher degree of conversion would result in less unreacted monomer ending up in the wastewater (McGrath et. al. 1979). While these rubbers would be harder to process, their processability could be improved by adding extender oils. This practice is widespread in the industry.

- Increased automation.
  Increased use of automation results in the reduction of errors and bad batches. This means a lower wash frequency and thus less waste.

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- Increase batch size to minimize cleaning frequency.

  Reducing equipment cleaning frequency by increasing batch size would result in less cleanup wastes. Expansion of production capacity is usually done by adding more batch reactors. By using a larger batch reactor, as opposed to two smaller batch reactors, the amount of waste generated from cleaning would be reduced. This trend, observed in the polyvinyl-chloride (PVC) industry, might prove economical in the synthetic rubber industry (Cameron, Lundeen, and McCulley Jr. 1980).

- Better operating practices.

  Usually, equipment is rinsed with large volumes of water to remove residual rubber. By initially rinsing the reactors with a small volume of water (about 5 percent of equipment volume), waste water with a high concentration of rubber particles is generated. This stream can then be recycled to the process. The equipment can then be washed with a full volume rinse and generate wastewater with a lower solid content. This two-step rinsing procedure was adopted by Borden Chemical Co. and reduced off-product waste by 95 percent (Sittig 1975b).

  A similar procedure was adopted by a plant for cleaning latex tanks. The plant used a rinse procedure that generated a rinse water containing more than 2 percent solids. This stream was then used for latex blending (Riley 1974). Rinse water containing less than 2 percent solids is not useful for blending.

9.1.3 Other Aqueous Wastes

These aqueous wastes are the result of inhibitor removal, coagulation and screening, rinsing and dewatering, carbon black slurry preparation, and monomer, solvent, and catalyst recovery steps. The removal of inhibitors from the monomers by caustic wash generates a waste containing traces of phenol. Since this stream is usually recycled to the washing process until it becomes saturated, the volume of this waste stream is quite small. The overflow from carbon black slurry preparation is also small and contains only the suspended carbon particles.

The bulk of the aqueous wastes are the result of coagulation and screening, rinsing and dewatering, and monomer, solvent, and catalyst recovery operations. All of these streams are usually sent to settling pits where suspended solids and heavy oils are removed. Since some of these aqueous streams contain significant amounts of organics (unreacted monomers, etc.), they may be steam stripped to remove volatile organics, incinerated, or stored in drums for land disposal. The following methods could reduce the generation of these aqueous wastes:

- Use of alternate coagulation procedures.
  Usually, coagulation of the latex produced by emulsion polymerization is achieved by the addition of brine and sulfuric acid solution. The overflow from the coagulation tank contains solid particles which are recovered in settling pits. This waste stream can be reduced by using alternate means of coagulation such as spraying the latex into a heated chamber and thereby accomplishing coagulating and drying the latex in one step. Another approach is to deposit the latex as a frozen film on rolls kept at low temperature followed by washing, using ultrasonic sound, or by forcing the latex through jets for emulsion breaking (Riley 1974). Since all of the above alternatives achieve coagulation without using increased quantities of water (brine and sulfuric acid solutions), less aqueous waste is produced.

  Using acid polyamide, a coagulation procedure that reduces the quantity of total dissolved solids in the overflow has been developed. This procedure was adopted by a synthetic rubber plant which reduced coagulation overflow wastes significantly. Also reported was a process used by another plant that converted rubber cement from solution polymerization directly into baleable crumbs using an extruder. This process was used for polybutadiene and reduced waste significantly since the traditional method of coagulation (using hot water or steam) was not required.

- Recycling of vacuum pump seal water.
  Vacuum pumps are used for generating vacuum in the light monomer recovery operation. The water used to seal the vacuum pump accumulates organics and is usually discharged as a waste stream. Studies have been done on recycling this aqueous waste to the polymerization process (op. cit.). Though the quantity of this stream is not known, this procedure could contribute to overall waste reduction.

- Different mode of carbon black slurry preparation.
  Usually, carbon black (in the form of a water slurry) is added to the polymer latex from the reactor. The overflow from the slurry mixer results in a wastewater stream. By using a different slurrying procedure, some plants have effectively reduced this loss (Riley 1974).

- Altering product composition.
  As discussed in section 9.1.2, changing the product composition could reduce the concentration of contaminants in the aqueous wastes.

- Alternatives to solution polymerization.
  Polyisoprene and polybutadiene are produced mostly by solution polymerization. Enoxy Chimica S.P.A. of Italy has developed a polymerization process which does not use solvents (Zimmerman 1981, Lipowicz 1982). The process uses a rare earth-based catalyst system at conventional temperatures and pressures. Currently, a pilot plant is in operation in Italy. The process has the advantage of eliminating the need for steam stripping the product which reduces the amount of wastewater generated. Additional advantages include energy savings up to 80 percent, a much smaller reactor, and reduction of heavy slops formation.

9.1.4 Heavy Ends and Waste Oils

Heavy ends are removed by the various distillation operations used for the recovery of monomers and solvents. This stream, sometimes referred to as "heavy slops", is usually disposed of by drumming for landfill or incineration. This potentially hazardous stream can be reduced by the following methods:

- Replace the slurry process for butyl rubber with a solution process.
  The slurry process for butyl rubber synthesis uses toxic methyl chloride as a carrier fluid, which ends up in the heavy slops (Parr, Parson and Philips 1977). Though it was suggested that a use could be found for this waste stream (Kushnir and Nagy 1978), this has not been supported by other sources. By employing a solution process using a solvent such as hexane or pentane, the toxicity of this stream could be reduced. A solution process of this type is believed to be in commercial operation in the USSR (Parr, Parson and Phillips 1977).

- Alternatives to solution polymerization processes.
  As mentioned in Section 9.1.3, a non-solvent process developeed by Enoxy Chimica S.P.A. can reduce formation of heavy slops in production of polyisoprene and polybutadiene.

- Avoiding the use of aromatic solvents.
  Aromatic solvents are usually more volatile and toxic in comparison to aliphatic solvents. By using aliphtic solvents, the toxicity of the heavy slops could be reduced (Parr, Parson, and Phillips 1977).

9.1.5 Spent Catalyst and Adsorbent

The catalysts used in emulsion polymerization usually stay in the final rubber product. In solution polymerization, the catalysts are removed by contacting the polymer slurry with an alcohol solution and then precipitating the catalyst from the alcohol (Kushnir and Nagy 1978). The separated catalyst, present as a suspension in an aqueous stream, is usually mixed with other aqueous wastes and sent to settling ponds. In these ponds, the catalyst (in the form of oxides of titanium or aluminum), separates out along with other suspended particles (rubber, carbon black, etc.). All of these solids are removed periodically and disposed of in a landfill. Since the spent catalyst waste is reported to be equal to about 0.01 percent of the total product, and since reducing this waste will not have a significant impact on overall waste generation, no waste reduction measures are proposed.

In solution polymerization processes, care is taken to keep water out of the system. This is accomplished by drying the monomer-solvent mixture with a solid desiccant. After several regeneration cycles, the desiccant is discarded as a waste. The actual disposal methods for this solid waste were not reported. Elimination of this stream can be accomplished, in principle, by using a distillation of the feed to remove water, as is done in the case of EPR. However, it is not clear that the resulting wastewater stream is environmentally preferable to the existing alternative. Further exploration of this approach is needed.

9.1.6 Spills and Leaks

Spills and leaks are the result of accidental discharges of liquids and solids in various parts of the plant. The exact amount of this stream is not known. The liquids are usually mixed with the heavy slops and disposed of as explained previously. The following suggestions could reduce this waste stream:

- Use of continuous operation instead of batch operation.
  Since there are many sequential processing steps in a batch operation, chances of operator errors that result in inadvertent spills and emissions are higher. Thus, a continuous operation is preferable.

- Better operating practices.
  Latex spills are usually washed down with water and are sent to the waste treatment plant. Washing with water makes coagulation of this stream difficult. By using alum to coagulate the latex in-situ and removing the coagulated rubber solids with scrapers, lower quantities of water are required for washing (Riley 1974). This reduces the quantity of wastewater generated due to washing of latex spills.

  Losses from loading and unloading procedures can be reduced by the following method. Two hoses are usually connected to the track of a railroad car for loading or unloading. The bottom hose transfers material while the top hose maintains pressure. Material left in the hoses may be lost or spilled upon disconnection. This can be avoided by more complete drainage and by purging the lines with inert gas to a recovery system or a control device prior to disconnect.

9.2 Implementation Profile

Some of the noted source control methods appear to be economically attractive. For example, by reusing off-grade products or by selling them at a lower price, off-grade product waste can be reduced, thereby cutting disposal costs and perhaps increasing revenue at the same time. Segregating wastes (e.g. keeping the spent catalyst stream separate from the coagulation overflow) involves little or no cost to the facility but

can mean substantial savings in disposal costs. Modifying equipment cleaning procedures results in recycleable waste streams generated with only minor increases in operating costs.

All other methods identified may require a significant expenditure of capital and an increase in labor costs. The economic feasibility of these methods depends upon their potential to produce a savings in disposal and treatment costs and reduce future liability for landfilled waste. Some of these methods may even be feasible for firms which have already installed wastewater treatment units, though managers at these firms are generally reluctant to consider further environmental expenditures. Even so, source reduction methods are certainly worth considering when planning for plant expansions or replacements.

Because of the diversity encountered in the synthetic rubber industry, source control methods feasible at one facility may not be feasible at another. In addition, one facility may produce many different grades of rubber, making it difficult for a general and yet meaningful control scheme to be profiled. In practice, managers of each facility must independently determine their own best course of action with regard to waste minimization.

9.3 Summary

The summary of all noted source control techniques is given in Table 9-1. Each technique was rated for its effectiveness, extent of current use and future application potential on scale of 0 to 4. The ratings were derived by project staff based on review of the available. The estimates of current level of waste reduction achieved (current reduction index) and possible future reduction (future reduction index) were obtained from the ratings in accordance with the methodology presented in the introduction to this appendix.

The current reduction index (CRI) is a measure of reduction of waste that would be generated if none of the methods listed were implemented to their current level of application. For the entire synthetic rubber industry, CRI is 2.1 (53 percent) which is indicative of the significant level of waste minimization that already has taken place.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE SYNTHETIC RUBBER MANUFACTURING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality	Effectiveness					Probable	Maximum
Off-Grade Products	1. Reduce polymer build-up on react wall	1	1	1	1	2		0.3	0.4	
	2. Use continuous versus batch operation	1	1	2	1	1		0.5	0 4	
	3. Increased automation	1	1	2	1	2		0.5	0.8	0 8
	4. Provide emergency backup systems	1	1	2	3	1		1.5	0.1	
	5. Find use for off-grade product	1	2	3	3	2		2.3	0 4	
	Overall	1.00	1.20	2.00	1 80	1.60	0.77	2.3	0.4	0.8
Equipment Cleaning Wastes	1. Reduce polymer build-up on react wall	1	1	2	1	2		0.5	0.8	
	2. Alter product composition	1	1	1	3	1		0.8	0.1	
	3. Increased automation	1	1	1	1	1		0 3	0 2	
	4. Increase batch size / reduce cleaning	1	1	2	2	1		1.0	0.3	
	5. Better operating practices	1	1	3	2	3		1.5	1.1	1 1
	Overall	1.00	1.00	1.80	1.80	1.60	0 04	1 5	0.5	1.1
Other Aqueous Wastes	1. Use alternate coagulation methods	2	2	3	1	2		0.8	1 1	1 1
	2. Recycle vacuum pump seal water	1	1	1	1	2		0.3	0 4	
	3. Different carbon slurry preparation	1	1	1	1	1		0.3	0.2	
	4. Alter product composition	1	1	1	3	1		0.8	0 1	
	5. Use alternatives to solution process	1	2	1	0	1		0 0	0.3	
	Overall	1 20	1 40	1.40	1 20	1 40	0.12	0 8	0 4	1 1
Heavy Ends and Waste Oils	1. Replace slurry process - Butyl rubber	1	1	2	1	1		0 5	0 4	0 4
	2. Use alternatives to solution process	1	1	1	0	1		0 0	0 3	
	3. Avoid the use of aromatic solvents	1	1	2	1	1		0 5	0.4	0 4
	Overall	1.00	1.00	1.67	0.67	1.00	0 06	0.5	0 3	0 4
Spills and Leaks	1. Use continuous versus batch operation	1	1	2	1	1		0.5	0 4	
	2. Better operating practices	1	1	3	2	3		1.5	1.1	1 1
	Overall	1 00	1 00	2 50	1 50	2 00	0 01	1 5	0.8	1 1
All Sources	All Methods							1.00	2 1	0 4	0.8

(*) These streams include listed "F" and/or "K" RCRA wastes.

The future reduction index (FRI) is an indication of the level to which the currently generated waste can be reduced if all of the techniques noted were implemnted according to their rated potential. The FRI value of 0.4 to 0.8 (10 to 20 percent) is indicative of a low to moderate extent of future waste reductions. Among the techniques that were found most effective and applicable (as evidenced by high FRI value) for the control of waste generation were increased automation, use of alternate coagulation methods, and further implementation of better operating practices.

10. PRODUCT SUBSTITUTION ALTERNATIVES

Synthetic rubbers are predominantly used in the manufacture of tires and tire products. It is estimated that tire replacement amounts to about 75 percent of total tire sales (Zanetti 1984a). By increasing the lifetime of passenger car tires, the demand for synthetic rubber can be decreased. This could be done by better consumer tire maintenance (e.g. by preventing tire under-inflation and by maintaining proper wheel-alignment), and by increasing car-pool use.

It is estimated that 92% of the passenger tires made in 1990 will be radial tires, up from 61% in 1980. Since radial tires use more natural rubber, the demand for synthetic rubber could decrease.

Natural rubber is an accepted substitute for synthetic rubber (the roles were reversed prior to 1940). Most of the natural rubber is imported; however, domestic rubber production from guayule plants (found in the southwestern U.S.) has received recent attention (McNaughton 1983, Lipowicz 1982). The concept of guayule rubber was explored in the U.S. during the Second World War when natural rubber imports declined drastically. Though guayule rubber lacks economic feasibility at present, it is expected to be economical by the end of this decade.

The increasing cost of styrene prompted manufacturers to investigate possible substitution of SBR by medium vinyl polybutadiene rubbers (Parr, Parson, and Phillips 1977). The waste reduction implications of this substitution are not clear.

EPR can be used for tire-making purposes, replacing other synthetic rubbers. Various problems associated with using EPR for tire applications have been solved (Parr,

Parson, and Phillips 1977). The apparent low waste loads associated with EPR makes this substitution worthy of exploration.

11. CONCLUSIONS

While the synthetic rubber industry has done much to reduce wastes, it appears that moderate reductions characterized by a future reduction index of 0.4 to 0.8 (10 to 20 percent) are possible. Several methods that appear to be quite effective would be to expand the reuse or recycle of off-grade products, increase the use of automation, use alternate coagulation procedures, and extend the application of good operating practices. Source reduction methods already in application at some plants need to be examined at others.

One area that can have an impact is improved tire maintenance by consumers which, in turn, could increase passenger car tire life and thus reduce the demand for synthetic rubber. By increased use of radial tires, the amount of synthetic rubber used per tire could be lowered since radials use more natural rubber than other types of tires. Natural rubber is the best substitute for synthetic rubber; however, full environmental assessment of such a substitution must be made, along with an evaluation of socioeconomic impacts, before its desirability is fully established.

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1. PROCESS: 1,1,1-TRICHLOROETHANE MANUFACTURE

2. SIC CODE: 2869(2)

3. INDUSTRY DESCRIPTION

Manufacturers of 1,1,1-trichloroethane (1,1,1-TCE) are included as part of the organic chemicals manufacturing industry. The industry is composed of relatively large plants producing a wide variety of chlorinated compounds. The manufacturing processes are often interrelated, since products from one process can be used as feedstock for another.

Three major companies are responsible for all of the U.S. production of 1,1,1-TCE. Dow Chemical is the largest producer of 1,1,1-TCE, with two plants providing 57 percent of the total U.S. production capacity. PPG Industries Inc. and Vulcan Materials Co., each with one plant, account for 27 percent and 16 percent of the total production capacity, respectively.

Three of the plants producing 1,1,1-TCE are located in Louisiana. The remaining operational site, owned by Dow, is located in Texas.

4. PRODUCT AND THEIR USE

Annual U.S. production of 1,1,1-TCE was 334,000 short tons per year in 1984 (Anonymous 1985a). 1,1,1-TCE is primarily used as solvent for oils, grease, and wax in metal cleaning operations. Commercial grades of 1,1,1-TCE are available with or without oxidation inhibitors added. Solvent degreasing grades often contain trace amounts of organic inhibitors, such as acid acceptors or metal stabilizers, which are used to neutralize any HCl formed during solvent use, and to deactivate metal surfaces for the prevention of adverse reactions during the cleaning process. 1,1,1-TCE is also used as raw material for the manufacture of other chlorinated chemicals, in aerosol propellant formulations, and as a solvent in adhesive and coating formulations. The relative consumption rates of 1,1,1-TCE are given in Table 4-1 based on 1977 data. The relative distribution of 1,1,1-TCE among the different end uses appears to have remained unchanged since that date.

Table 4-1 End-Use Profile for 1,1,1-TCE in the U.S.

End Use	Relative Consumption Rate Percent
Metal Cleaning	67.0
Chemical Intermediate	2.0
Miscellaneous	31.0
Total	100.0

Source: Organic Chemicals Manufacturing (Key et al. 1980).

5. RAW MATERIALS

The raw materials used to produce 1,1,1-TCE are summarized below (Van Gemert 1982, Stevens 1979, Key et al. 1980):

Reactants: hydrogen chlorine, chlorine, vinyl chloride, 1,1-dichloroethylene (VCM route).
ethane, vinylidene chloride (ethane route).

Catalysts: $FeCl_3$

Inhibitors: butylene oxide, dioxane, nitro methane, tert-amyl alcohol, methyl ethyl ketone, isopropyl nitrate

Neutralizers: ammonia, sodium hydroxide

6. PROCESS DESCRIPTION

Production of 1,1,1-TCE in the United States is based primarily on the two-step chlorination process using vinyl chloride as a raw material. This method accounts for 85 percent of total production. An alternative production method, based on the direct chlorination of ethane, is responsible for the remaining 15 percent. The ethane process, however, is also capable of using ethylene dichloride derivatives as feedstock. Detailed descriptions of the two processes mentioned are given elsewhere (Boozalis and Ivy 1978, Berrie, Chaler, and Chuffart 1978, Key et al. 1980). Due to its wider applicability, only the vinyl chloride route will be discussed.

In this process, vinyl chloride is first catalytically hydrochlorinated to give 1,1-dichloroethane (1,1-DCE). The 1,1-DCE intermediate is then thermally chlorinated to give 1,1,1-TCE as the final product. Yield from vinyl chloride often exceeds 95 percent. The overall reactions include:

1. Hydrochlorination of vinyl chloride to 1,1-DCE

$$CH_2 = CHCl + HCl \xrightarrow[\text{catalyst}]{FeCl_3} CH_3\text{-}CHCl_2$$

2. Chlorination of 1,1-DCE to 1,1,1-TCE:

$$CH_3\text{-}CHCl_2 + Cl_2 \longrightarrow CH_3CCl_3 + HCl$$

Figure 6-1 represents the flow diagram for the production of 1,1,1-TCE from vinyl chloride. For this process, vinyl chloride, HCl, and recycled chlorinated hydrocarbons are fed into a hydrochlorination reactor, operating at 95°F-105°F. The reaction is homogeneously catalyzed by dissolved ferric chloride. Ammonia is then added to the reactor effluent stream to form a solid complex with the residual HCl and the $FeCl_3$ catalyst.* The complex is removed through a spent catalyst filter as solid waste. The filtered hydrocarbon stream then passes through a heavy ends column. Bottoms from this column, containing tars and heavy chlorinated hydrocarbons, are removed as a liquid waste. The overhead is transferred to a light ends column for the separation of 1,1-DCE. Overhead from the light ends column, containing mostly unreacted vinyl chloride, is recycled to the hydrochlorination reactor. The 1,1-DCE intermediate is removed as bottom from the distillation column and is stored for further processing.

In the second stage of the process, 1,1-DCE and chlorine are combined and fed to a non-catalytic fluidized bed chlorination reactor, operating at 750°F. The exothermic reaction is thermally induced and subsequently self-sustaining. The reactor effluent then passes through an HCl column, where HCl and light chlorinated hydrocarbons are removed as overhead. This stream can be used directly to supply HCl for the manufacturing of other chlorinated chemicals, or is further purified to recover HCl as a by-product.

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* Other means of $FeCl_3$ removal, which do not involve NH_3 addition, are also practiced.
Dow Chemical Co. 1985: Personal communication.

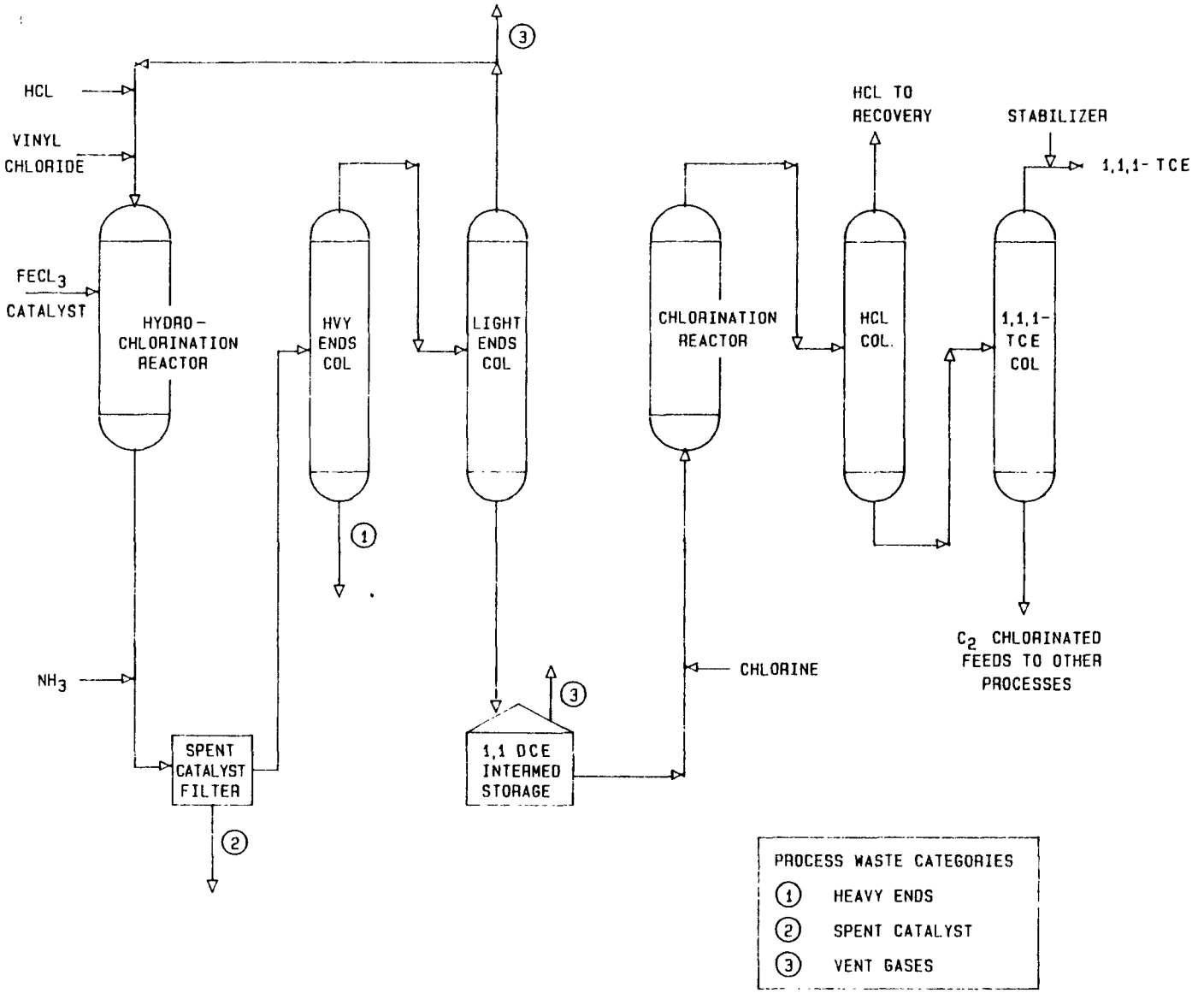

Figure 6-1 Production of 1,1,1-TCE from Vinyl Chloride

The bottom stream from the HCl column is fed to the 1,1,1-TCE column, where the purified 1,1,1-TCE is removed as overhead. Inhibitors are then added to provide different commercial grades of the final product. The bottom stream from the 1,1,1-TCE column, containing mostly C_2 - chlorinated hydrocarbons, is often transferred as feed to other chlorination processes. Storage tanks and light ends off distillation column overheads are vented to a scrubber to remove residual HCl and chlorinated hydrocarbons, although alternate means of processing are also used.

7. WASTES DESCRIPTION

The primary specific wastes associated with the 1,1,1-TCE manufacturing industry are listed in Table 7-1. The waste streams generated from this industry include liquid organic wastes, semi-solid spent catalyst, and scrubbing system wastewater.

Since liquid organic effluents, such as heavy tars, are often used as a feedstock to other processes in a highly integrated chlorohydrocarbon facility, the term "waste" is not applicable universally. Organic heavy ends account for a large portion of the residuals generated. This liquid stream comes from the distillation of the hydrochlorination reactor effluent stream to remove heavy chlorinated hydrocarbons that cannot be directly recycled or further processed. The resulting tars are often oxidized for recovery of HCl and heat or sent to land disposal.

Another major source of waste comes from the removal of spent catalyst which is used for the hydrochlorination reaction. Ammonia is added to the reactor effluent stream to form a solid complex with the catalyst. The solid is then filtered out, and the resulting sludge is sent to land disposal. Again, it must be noted that certain facilities use alternate methods of catalyst removal which do not rely on NH_3 addition.

The scrubber effluent, containing mostly water with condensed or dissolved halogenated organics, is normally sent to a central wastewater treatment system for the entire facility.

Table 7-1 1,1,1-TCE Manufacturing Process Wastes

No.	Waste Description	Process Origin	Composition	RCRA Code
1.	Heavy ends	Hydrochlorination reactor	tars, heavy chlorinated hydrocarbons	K096
2.	Spent catalyst	Spent catalyst filter	$FeCl_3$, ferric ammonium chloride complex, dichloroethene	K028
3.	Scrubber effluent waste	Emission control operations	chlorinated hydrocarbons, water	--
4.	Equipment cleaning wastes	Tanks, towers, heat exchangers	--	F024
5.	Spills & leaks	--	--	--

8. WASTE GENERATION RATES

The survey of the available literature did not yield waste generation rates from the production of 1,1,1-TCE. Fractional waste generation (the percentage each stream represents of the total waste generated) was estimated by the report authors based on the available information and industry comments. These values are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" have also been included. Good operating practices are defined as procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel practices
  - Management initiatives
  - Employee training
- o Procedural measures
  - Documentation
  - Material handling and storage
  - Material tracking and inventory control
  - Scheduling
- o Loss prevention practices
  - Spill prevention
  - Preventive maintenance
  - Emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified. A summary of the waste sources and the corresponding source reduction methods is given in Table 9-1. This section describes the listed methods, including known specific applications.

9.1.1 Heavy Ends

A major portion of the waste generated from the manufacturing of 1,1,1-TCE comes from the distillation operation required for the removal of chlorinated compounds containing more than two carbon atoms. These compounds are formed by various polymerization reactions during the hydrochlorination of vinyl chloride to form the 1,1-DCE intermediate. Since these compounds cannot be directly recycled, or readily used as feedstock to other manufacturing processes, they must be chemically converted prior to reuse or produced in minimum quantities prior to disposal. The following minimization techniques were noted:

- o Heavy ends hydrocracking.
  Similarly to the method proposed in the process study for TCE/PCE manufacturing, an additional reactor might be used to hydrocrack the heavy chlorinated hydrocarbons into lighter products. The light chlorinated

organics generated from this step can then be recycled to the hydrochlorination reactor. The experiments at the Illinois Institute of Technology revealed severe catalyst fouling problems. Further research is planned to explore other operating conditions such as the effect of increasing H_2/feed ratios to alleviate the fouling problem*.

- o Lowering hydrochlorination reactor temperature.
  It is possible that the heavy ends formation reaction has a higher activation energy than the principal 1,1-DCE formation reaction. If this is true, then the selectivity ratio would increase with a decrease in temperature. This would lead to higher yields of 1,1-DCE and, consequently, lower generation of heavies. Examination of the reaction kinetics along with the economic feasibility of this proposed method appears worthwhile.

- o Thermal oxidation with recovery of HCl and heat.
  This technique is used by at least one facility**. The heavy ends are combusted and both heat and HCl are recovered. Recovered hydrochloric acid can either be sold or used to generate anhydrous HCl for use in other processes.

9.1.2 Hydrochlorination Catalyst Waste

Waste is produced from the disposal of spent catalyst from the hydrochlorination reactor. For the facilities where $FeCl_3$ catalyst (dissolved in the 1,1-DCE liquid effluent from the reactor) is treated with ammonia to form solid complexes, the following source reduction methods were noted:

- o Elimination of filter aid.
  The type of filters used to separate the precipitated salts from the organic stream was not described in the available literature. In cases where precoat type pressure filters are being used, a filter aid is first deposited to improve the filtration rate. Waste volumes can be significantly reduced by switching to bag or leaf type filters which do not require the use of a filter aid (LWVM 1985).

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* Illinois Institute of Technology 1985: Personal communication.
** Dow Chemical Co. 1985: Personal communication.

- o $FeCl_3$ catalyst precipitation and recycle.
  Decreasing the temperature of the 1,1-DCE liquid effluent stream may cause $FeCl_3$ to precipitate because of the decrease in solubility. The precipitated catalyst can then be separated, redissolved, and recycled back to the reactor. Residual catalyst in the 1,1-DCE stream can then be removed conventionally using ammonia.

9.1.3 Equipment Cleanup Wastes

Usually, the wasteloads associated with equipment cleaning are small and periodic in nature (once every 1 or 2 years). Further reductions may be obtained through:

- o More complete drainage of process piping or equipment prior to cleaning.

- o Lower process film temperatures and increase turbulence at the heat exchange surfaces to reduce fouling rates. This can be accomplished by avoidance of overdesign and using recirculation during turndown operations.

- o Use of electropolished or Teflon* heat exchanger tubes to reduce deposit clingage (Anonymous 1985c).

- o Use of in-process heat exchanger tube cleaning devices (Anonymous 1985b).

The reader is also referred to the study of process equipment cleaning contained in this appendix.

9.1.4 Spills and Leaks

As mentioned before, spills and leaks constitute a very minor waste stream owing to the extensive implementation of preventive maintenance measures in facilities dealing

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* Registered trademark of E.I. Du Pont de Nemours & Co.

with hazardous materials. Further source reduction is possible, in principle, through better operating practices (see also process study entitled "Good Operating Practices"). Additionally, some consideration should be given to:

- o Replacing single mechanical seals with double mechanical seals on pumps or using canned seal-less pumps.
- o Using leak detection systems and portable monitors.
- o Using enclosed sampling and analytical systems.
- o Using vapor-recovery systems for loading, unloading, and equipment cleaning.

9.2 Implementation Profile

The facilities that currently combust their organic wastes with attendant recovery of HCl and heat value will probably have little or no incentive to pursue waste minimization options, some of which may require considerable investment of effort for engineering and economic analyses before implementation.

9.3 Summary

Table 9-1 represents a summary of source control methodologies for the 1,1,1-trichloroethane manufacturing industry. Based on the measures currently taken to minimize waste, it is estimated that waste generation has been reduced to the level characterized by a current reduction index of 3.0 (75 percent), due to the implementation of methods listed in this section (the 75 percent value represents the amount of waste that current waste reduction measures have reduced compared to the waste volumes that currently would be generated without these measures.) By implementing additional waste reduction measures, it appears that the amount of waste currently being generated can be further reduced to a level characterized by an index of 0.7 to 0.8 (18 to 20 percent reduction from current waste generation levels.) The most effective potential measures for achieving this reduction are those with high future reduction index shown in Table 9-1. These include: hydrocracking the heavy chlorinated hydrocarbons, precipitation and recycling of the $FeCl_3$ catalyst. Among the measures that do have current industrial precedent, thermal oxidation of the heavy ends with attendant HCl and heat recovery has the highest application potential.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE 1,1,1 - TRICHLOROETHANE MANUFACTURING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Heavy Ends (*)	1. Hydrocrack heavy chlor. hydrocarbons	1	1	3	0	1		0.0	0.8	0.8
	2. Use lower hydrochlor. reaction temp.	0	0	2	0	1		0.0	0.5	
	3. Recover HCl/heating values	2	2	4	3	3		3.0	0.8	0.8
	Overall	1.00	1.00	3.00	1.00	1.67	0.89	3.0	0.7	0.8
Spent Catalyst (*)	1. Eliminate use of filter aid	0	0	2	1	1		0.5	0.4	
	2. Precipitate & recycle FeCl3 catalyst	0	0	3	0	1		0.0	0.8	0.8
	Overall	0.00	0.00	2.50	0.50	1.00	0.05	0.5	0.6	0.8
Equipment Cleaning Wastes (*)	1. Increase equipment drainage time	1	1	3	3	2		2.3	0.4	
	2. Lower heat exchanger film temperature	1	1	2	1	1		0.5	0.4	
	3. Electropolish heat exchanger tubes	2	1	3	0	2		0.0	1.5	1.5
	4. Use in-process H.X. cleaning devices	2	1	2	1	2		0.5	0.8	
	Overall	1.50	1.00	2.50	1.25	1.75	0.05	2.3	0.8	1.5
Leaks and Spills	1. Use double mechanical seals on pumps	1	1	3	4	2		3.0	0.0	
	2. Use leak detectors	3	3	2	3	1		1.5	0.1	0.1
	3. Enclosed sampling and analy. systems	3	2	2	3	1		1.5	0.1	0.1
	4. Use of vapor recovery systems	2	2	4	4	1		3.9	0.0	
	Overall	2.25	2.00	2.75	3.50	1.25	0.01	3.9	0.1	0.1
All Sources	All Methods							1.00	3.0	0.7	0.8

(*) These waste streams include listed "f" and/or "K" RCRA wastes.

10. PRODUCT SUBSTITUTION ALTERNATIVES

The growth in industrial use of 1,1,1-TCE as a solvent for vapor degreasing and cold cleaning operations has been substantial in the 1970's and the early 1980's. Due to its relatively low toxicity, low level of photochemical reactivity, its adequate solvency, and the absence of the need for equipment changeover, 1,1,1-TCE was used extensively to replace the more highly criticized trichloroethylene as a solvent for metal cleaning operations. Environmental concerns over the fact that 1,1,1-TCE may threaten the earth's stratospheric ozone layer, however, has placed the use of 1,1,1-TCE under stricter scrutiny (SRI 1982).

Substitution of water-soluble synthetic cleaners for organic solvents has also been practiced in industry. Improvement in cleaning techniques can enhance the ability of weaker cleaning substances, such as alkaline solutions or soaps, to remove oily residues. These less toxic cleaners can then be used to replace chlorinated organic solvents such as 1,1,1-TCE.

Production demand for solvents (including 1,1,1-TCE) is largely controlled by the consumers' effort for conservation and the extent of solvent recovery being employed. Increasing costs of waste disposal, coupled with stricter air emission regulations, are likely to result in increased recycling and tighter control of solvent evaporation losses. Conservation and recovery, together with availability of less toxic substitutes, may result in a future reduction of the production rate of 1,1,1-TCE.

11. CONCLUSIONS

The principal waste stream from the 1,1,1-TCE production process consists of chlorinated organic by-products (heavy ends), which are formed during the synthesis stage. Past modifications of the manufacturing process to eliminate the formation of by-products were not in evidence; instead the trend has been to reprocess this stream. In facilities where heavy ends are currently dealt with satisfactorily by thermal oxidation combined with HCl and heat recovery, manufacturers of 1,1,1-TCE do not have the incentive to change their manufacturing process. Further extension of this option (thermal oxidation) appears to be a major practical step toward minimizing waste disposal. Nevertheless, source reduction techniques, such as heavy end hydrocracking with recycle, may deserve further investigation primarily as yield promoters and not necessarily as waste minimizers.

It appears that, in the case of 1,1,1-TCE, the issue of reducing wastes related to manufacturing process is subordinate to the issue of product substitution or use alteration relying on more extensive use of improved cleaning techniques, employment of less toxic cleaning substitutes and increased recovery and conservation efforts by the users. This conclusion is based on the observation that nearly two-thirds of the total 1,1,1-TCE produced is consumed in cleaning operations and subsequently disposed of as cleaning sludges or lost as atmospheric emissions. By comparison, the amount of wastes produced during the manufacturing process is very minor.

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13. INDUSTRY CONTACTS

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1. PROCESS: TRICHLOROETHYLENE/PERCHLOROETHYLENE MANUFACTURE

2. SIC CODE: 2869(2)

3. INDUSTRY DESCRIPTION

Manufacturers of trichloroethylene (TCE) and perchloroethylene (PCE) are included as part of the organic chemicals industry. A variety of feedstocks and processes are used to manufacture TCE and PCE as co-products.

3.1 Company Size Distribution

Four major manufacturers are currently responsible for all of the U.S. production of TCE and PCE. These are large chemical companies producing a great variety of organic compounds at each of their manufacturing plants. A company usually owns one or two plants, with combined annual production capacity of TCE and PCE between 25 to 200 thousand short tons/year (TPY).

3.2 Principal Producers

The five principal producers of TCE and/or PCE are listed below*:

Diamond Shamrock Corp. - PCE only
Dow Chemicals USA - TCE/PCE
E.I. du Pont de Nemours & Company, Inc. - shut down
PPG Industries - TCE/PCE
Vulcan Materials Company - PCE only

3.3 Geographical Distribution

Nationwide, there is a total of six plants producing TCE and/or PCE (SRI 1982). Among these, one plant is located in Texas, three in Louisiana, one in Kansas, and one in California.

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* PPG Industries 1985: Personal communication.

4. PRODUCTS AND THEIR USE:

TCE and PCE are used mainly as solvents for dry-cleaning and metal degreasing operations. PCE is also used as an intermediate for the production of other chemicals such as C_2-fluorocarbons. The end-use profile of TCE and PCE in 1981-1982 is given in Table 4-1. Due to stricter government regulations on the use of toxic solvents, consumption of TCE in metal cleaning was expected to drop by an average of 3% annually in the 1980's. While annual production rates of TCE in recent years could not be found, significant reduction from the value of 133,100 TPY produced in 1975 is expected due to the effect of increasing application of solvent re-use, recovery, and recycling. Demand for PCE peaked in 1979, but has been declining since. Annual U.S. production of PCE was 254,364 TPY in 1984 (Anonymous 1985).

Table 4-1. 1981-82 End-Use Profile for TCE/PCE in the U.S.

End Use	Relative Consumption Rates, %	
	TCE (a)	PCE (b)
Metal Cleaning	66	21
Dry Cleaning/Textile Processing	--	59
Chemical Intermediate	7	6
Miscellaneous	27	14
Total	100.0	100.0

Source: Hughes, et al., 1985

5. RAW MATERIALS

The raw materials used in the production process (Liepins et. al., 1977) are:

Reactants	ethylene chloride, ethylene dichloride, C_1-C_3 hydrocarbons, C_2-chlorinated hydrocarbons, chlorine, hydrochloric acid, oxygen (air)
Catalysts	$CuCl_2$, $BaCl_2$, KCl, $AlCl_3$, graphite, activated carbon.
Stabilizers	trimethylamine, pyrrole-based compounds, hydroquinone monomethyl ether, p-tertiary annyl phenol.

Neutralizers	sodium hydroxide, ammonia
Drying materials	sulfuric acid, molecular sieves, activated carbon, alumina gel, silica gel, and others

6. PROCESS DESCRIPTION

A variety of feedstocks and processes can be used to produce TCE and PCE. The principal processes of current commercial importance in the U.S. are:

- The coproduction of PCE and carbon tetrachloride (CCl_4) from the thermal chlorination of C_1 to C_4 paraffinic hydrocarbons, or their partially chlorinated derivatives.

- The coproduction of TCE and PCE from the thermal chlorination of ethylene dichloride (EDC), or other C_2-chlorinated hydrocarbons.

- The coproduction of TCE and PCE from the oxychlorination of EDC, or other C_2-chlorinated hydrocarbons.

These processes allow for re-use of C_3 and higher chlorinated hydrocarbon by-products, and thus enable the upgrading of chlorinated hydrocarbon residuals from other processes, with the exception of chlorinated tars*.

The thermal chlorination process can be performed either with or without a catalyst, and results in an output of HCl as a co-product. The catalytic oxychlorination process, on the other hand, avoids a net production of HCl and even provides an outlet for unwanted HCl from other processes. The oxychlorination reaction produces water along with TCE/PCE and hence requires the removal of water from the final product.

Descriptions of the above manufacturing processes have been given in the literature (McNeill Jr., 1979; Key et al., 1980; Liepins et. al., 1977). In this report, only the oxychlorination route will be described and discussed in detail.

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* E.I. Du Pont de Nemours & Co. 1985: Personal communication.

TCE and PCE are coproduced from the oxychlorination of EDC or other C_2-chlorinated hydrocarbons. The raw material ratios determine the proportions of TCE and PCE being produced. Conversion of chlorinated hydrocarbons to TCE and PCE was reported as 75-85%, with 10-15% chlorinated by-products, and 5-10% loss as CO and CO_2 (McNeill 1979). The overall reaction for this process is given by:

$$C_2\text{-chlorinated hydrocarbons} + O_2 + Cl_2 \xrightarrow{\text{catalyst}} TCE + PCE + H_2O \quad (1)$$

HCl can also be used as a feedstock since Cl_2 can be produced from HCl by a Deacon reaction:

$$2HCl + 1/2O_2 \xrightarrow{\text{catalyst}} Cl_2 + H_2O \quad (2)$$

Figure 6-1 represents the flow diagram for the production of TCE and PCE by oxychlorination. In this process, EDC, recycled chlorinated hydrocarbons, chlorine, and oxygen are fed into a fluidized bed reactor. For this process, C_2-chlorinated hydrocarbon wastes from other processes can also be consumed by introducing them into the organic recycle storage tank which feeds the fluid bed reactor. The reactor operates at slightly above atmospheric pressure and about 800°F (Keil 1979). The most common catalyst used is $CuCl_2$.

The reactor effluent gas, containing chlorinated organics, water, a small amount of HCl, CO, CO_2, and traces of other inert gases, is condensed using water-cooled and refrigerated condensers. The condensed crude product stream is drained through a decanter to remove entrained catalyst fines. The non-condensed vent gas stream is sent through a HCl recovery unit where the gas stream is water scrubbed to remove HCl as by-product.

The crude hydrocarbon stream is separated in the decanter. This stream is then azeotropically distilled to remove water. Waste water from the azeotropic distillation is combined with the aqueous phase containing catalyst fines from the decanter. The combined stream is sent to waste water treatment. An alternative approach relies on concentrated sulfuric acid (98% H_2SO_4) to remove water from the crude TCE/PCE. The acid and crude TCE/PCE are contacted and then allowed to separate. The acid is then sent to a vacuum flash unit where the absorbed water is removed. The water can then be steam- or air-stripped of organics (which are recycled to the reactor), pH

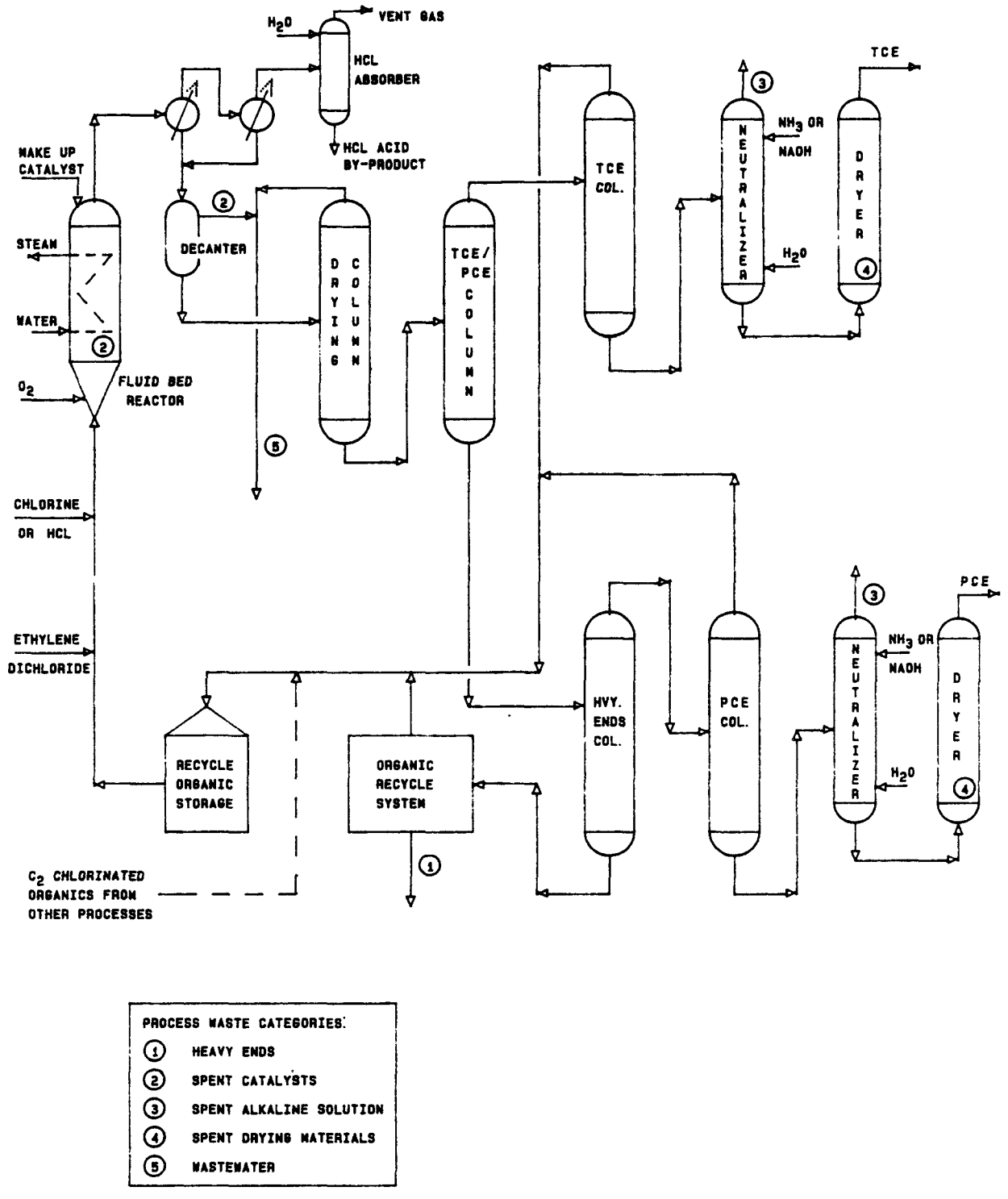

Figure 6-1 Production of TCE and PCE by Oxychlorination

adjusted and discharged to NPDES permitted outfall. The recovered sulfuric acid ($\sim$ 80% H_2SO_4) is then used in other processes or sold, e.g. as a raw material to produce fertilizer.

The crude chlorinated hydrocarbon mixture is further separated into TCE and PCE crude streams in a TCE/PCE column. The TCE crude is purified in a TCE column. Overhead from this distillation column is sent to an organic recycle storage tank. The bottom stream is neutralized with dilute caustic, ammonia or washed with water, and subsequently dried to give the desired TCE product. Wastes from the neutralization and drying operations are sent to waste-water treatment or disposal.

The bottom stream from the TCE/PCE column is separated in a heavy-ends column. The PCE-rich overhead stream from the heavy-ends column is sent to the PCE column where final PCE purification takes place. The overhead from the PCE column is recycled to the process and the purified PCE is withdrawn as bottoms, then neutralized, washed and dried.

The bottom stream from the heavy-ends column is flashed to separate the tars and carbon in the organic recycle system. The flash overhead stream is recycled back to the process. The separated heavies, called "hex-waste", contain hexachlorobenzene, hexachlorobutachrene plus various chlorinated C_2 compounds in addition to tars and carbon.

7. WASTE DESCRIPTION

The primary specific wastes associated with TCE/PCE manufacturing using the oxychlorination process are listed in Table 7-1. Organic heavy ends account for a large portion of the waste generated. This liquid stream comes from the distillation of the hydrochlorination reactor effluent stream to remove heavy chlorinated hydrocarbons that cannot be recycled or further processed. The resulting tars are often oxidized for recovery of HCl and heat or sent to land disposal.

A second source of waste involves spent catalyst. Entrained catalyst fines are removed from the reactor effluent stream when the condensed stream is drained through the decanter. The liquid waste stream is then combined with wastewater from

the azeotropic distillation or sulfuric acid drying operation, and is sent to wastewater treatment. Spent sulfuric acid is then used elsewhere in the facility or sold.

Neutralization and drying operations produce streams containing aqueous caustic solutions and spent absorbents. The aqueous waste streams are sent to waste water treatment, and the spent absorbent is regenerated (if a regenerable type is used) or land disposed.

The remaining portion of the waste is the scrubber effluent wastewater. This liquid waste stream is generated from the use of emission control equipment to limit the amount of gases being released to the atmosphere. The main sources for emission include vents from drying and neutralizing columns, vents from the HCl absorbent unit, and vents from organic storage tanks. The gas streams are often water scrubbed to remove hazardous materials. The resulting aqueous waste streams are combined and sent to wastewater treatment.

Table 7-1. TCE/PCE Manufacturing Wastes from the Oxychlorination TCE/PCE Process

No.	Waste Description	Process Origin	Composition	RCRA Code
1.	Heavy ends	Distillation from organic recycle system	Tars, heavy chlorinated hydrocarbons	K030
2.	Spent catalyst	Decanting of entrained catalyst	Metals, tars, chlorinated hydrocarbons	
3.	Spent caustic solution	Neutralization	Chlorinated hydrocarbons, spent caustic solution	--
4.	Drying waste	Drying operations	Spent absorbents	
5.	Spent scrubber wastewater	Emission control operations	Chlorinated hydrocarbons, acids, water	
6.	Equipment cleanup wastes	Cleaning of tanks, towers, and heat exchangers	--	F024
7.	Spills & leaks	--	--	--

8. WASTE GENERATION RATES

Very little data was available on waste generation rates from TCE/PCE manufacturing facilities. In 1975, Catalytic Inc. reported waste generation rates for the production of PCE from a generalized model plant. These values, however, were given for the manufacturing of PCE based on the direct chlorination process alone. Due to the lack of information, estimation of current annual waste generation volumes by the TCE/PCE manufacturing based on oxychlorination process could not be made. Fractional waste generation (weight fraction each waste represents as compared to all waste generated) was estimated by the project staff. These values are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" has also been included. Good operating practices are defined as being procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practices:

- o Waste Stream Segregation
- o Personnel Practices
  - Management Initiatives
  - Employee Training
- o Procedural Measures
  - Documentation
  - Material Handling and Storage
  - Material Tracking and Inventory Control
  - Scheduling
- o Loss Prevention Practices
  - Spill Prevention
  - Preventive and Corrective Maintenance
  - Emergency Preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified. A summary of the waste sources and the corresponding source reduction methods is given in Table 9-1. This section deals with the description of the listed methods, including known application cases.

9.1.1 Heavy Ends

A major portion of the waste generated from the manufacturing of TCE and PCE comes from distillation and flashing operations required for the removal of chlorinated hydrocarbon heavy ends. Since only light chlorinated hydrocarbons can be recycled to give TCE and PCE as products, reduction of the waste load can be done either through modifications of the existing manufacturing process to minimize the formation of heavy chlorinated hydrocarbons, or from the upgrading of these heavy by-products. The following source reduction methods are noted:

- Rapid cooling of reactor effluent gas.
  It is postulated that the extent to which the formation of the undesirable byproducts can be inhibited depends, in part, on how quickly the reactor offgas is cooled. This postulate is based on the argument that after leaving the fluid bed, the gas mixture is no longer in intimate contact with the catalyst. Therefore, side reactions can now take place without the benefit of selectivity control of the catalyst.

  Rapid quench of the reactor offgas leaving catalytic reactors is a feature often encountered in chemical processes, such as acrylonitrile or TCE/PCE production through thermal chlorination. It is suggested that the control of cooling (or quench) rate be examined in the context of reducing formation of the compounds found in the "hex-waste", along with the effects on TCE/PCE distribution.

- Control of chlorine-to-hydrocarbon ratio in the feed.
  Formation of C_3 and heavier compounds is strongly dependent on the chlorine-to-hydrocarbon ratio in the feed, as chlorine presence moderates carbon-to-carbon radical reactions responsible for the formation of C_{3+} byproducts. Examination of Cl_2/hydrocarbon ratio as a waste generation control parameter is suggested.

- Re-examination of fluidization conditions.

  In the fluidized beds operating in a bubbling regime, the effective size of bubbles controls the degree of mixing, which, in turn, influences the catalyst-gas contacting, represented by an interchange coefficient (Froment & Bischoff 1979). It is postulated that by decreasing the bubble size (e.g. by decreased tube pitch of the cooling coil bundle) the catalyst-gas contacting is improved resulting in a lower rate of formation of undesirable byproducts. It is suggested that this aspect be examined for its waste minimization potential.

- Application of improved catalysts.

  Use of the oxychlorination catalysts with higher selectivity toward TCE/PCE is an effective method of minimizing waste due to formation of undesirable byproducts. Research efforts have been made to improve currently used catalysts.

- Heavy ends hydrocracking.

  An additional reaction may be used to break the heavy chlorinated hydrocarbons into lighter products. The cracking can be done using catalytic hydrogenation processes. The light hydrocarbons generated from this operation can then be combined with other light chlorinated organic streams to be recycled to the reactor. Research work at the Illinois Institute of Technology indicates that the process remains, so far, technically infeasible due to severe fouling of the catalyst*. However, further research is planned to explore the effect of increasing H_2/feed ratio on reactor performance.

- Replacement of oxychlorination with a combination of direct chlorination and an HCl oxidation unit.

  Since the product yields from oxychlorination process ($\sim$ 80%) are usually much lower than those from direct chlorination processes ($\sim$ 95%), the use of chlorination instead of oxychlorination to manufacture TCE and PCE should reduce the amount of byproducts formed. Also, subsequent product purification operations are simpler because of the absence of water being formed as byproduct in an organic environment in oxychlorination step.

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* Illinois Institute of Technology 1985: Personal communication

A major disadvantage in using the chlorination process is the large amount of HCl that is formed as a byproduct. The HCl stream, however, can be electrolytically oxidized into H_2 and Cl_2. The chlorine generated in this process can then be recycled to the feed. Conversely, HCl can be directly oxidized using oxygen to H_2O and Cl_2 (Kel-chlor process). Both HCl oxidation routes have been applied commercially. A big problem is that the direct HCl oxidation route is very costly and, at the present, cannot compete with the conventional oxychlorination route. The only operating unit in the U.S. (Du Pont's Kel-Chlor facility in Corpus Christi, TX.) is planned to be shut down and replaced with oxychlorination due to unacceptably high cost. However, the electrolytic route is still under consideration*.

- Thermal oxidation with recovery of HCl and heat.
  The heavy ends are often incinerated and both heat and HCl are recovered. Recovered hydrochloric acid can either be sold or used to generate anhydrous HCl for use in the oxychlorination process.

9.1.2 Spent Catalyst

Hazardous waste can be produced from the periodic disposal of spent catalyst, or from the loss of catalyst due to entrainment. To reduce the waste load generated, the following steps can be taken:

- Use dry dust collectors or filters.
  High temperature ceramic fiber** or sintered metal can be used as filter elements to remove entrained catalyst fines from the effluent gas. The catalyst can be partially recycled back to the process or collected separately from other waste streams. The advantages include nearly complete removal of solids in the dry phase, which decreases waste generation associated with liquid filtration. The disadvantages may include longer residence time of reactor offgas in the stand-alone filter as opposed to currently used cyclones and the potential for plugging.

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* Du Pont 1986: Personal communication.
** Acurrex Corporation 1985: Personal communication.

- Use of a tougher catalyst support.

  In fluidized bed catalytic reactors, it is evident that the catalyst particles break into smaller fragments due to attrition and are consequently swept out of the reactor with the effluent gas. This results in the loss of expensive catalyst material and additional waste residual that must be disposed of. A substantial reduction in these losses might be obtained using a tougher catalyst support and/or by reducing the velocity of gas jets out of the distributor.

9.1.3 Spent Caustic Solution

Caustic wastes are generated in the TCE and PCE neutralization process where large amounts of water and ammonia are used. A method to reduce the toxicity of this stream as opposed to its volume was identified*:

- Use of NaOH instead of NH_3.

  The usual method of treating the spent caustic stream is to neutralize it using spent sulfuric acid and to then send it to wastewater treatment. Depending on the type of treatment system employed, the presence of copper in the stream can have adverse effects. Facilities using copper chloride catalysts would be advised against using ammonia since it will solubilize copper from the catalyst and create potential upsets downstream. This effect also points out the importance of efficient catalyst recovery back at the reactor and decanter units. According to industry contacts, most facilities are already using NaOH.

9.1.4 Drying Waste

The waste generated from the disposal of spent absorbent from the drying operation can be reduced by using regenerable drying materials which include activated carbon, aluminum gel, and silica. Regenerable drying agents are currently in wide use*.

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* E.I. Du Pont de Nemours & Co. 1985: Personal communication.

9.1.5 Equipment Cleanup Wastes

Usually, the wasteloads associated with equipment cleaning are small and periodic in nature (once every 1 or 2 years). Further reductions may be obtained through:

- o More complete drainage of process piping or equipment prior to cleaning.
- o Lower process film temperatures and increased turbulence at the heat exchange surfaces to reduce fouling rates.
- o Use of electropolished or Teflon* heat exchanger tubes to reduce deposit clingage (Anonymous 1985b).
- o Use of in-process heat exchanger tube cleaning devices (Anonymous 1985a).

All suggestions listed above will have only a minor impact on overall waste generation, since equipment cleaning wastes are but a small fraction of the total waste.

9.1.6 Spills and Leaks

As mentioned before, spills and leaks constitute a rather minor waste stream owing to extensive implementation of preventive maintenance measures in facilities dealing with hazardous materials. Further source reduction is possible, in principle, through better operating practices (see practice study entitled "Good Operating Practices"). Additionally, some consideration should be given to:

- o Replace single mechanical seals with double mechanical seals on pumps or use canned seal-less pumps.
- o Use of leak detection systems and portable monitors.
- o Enclosed sampling and analytical systems.
- o Use of vapor-recovery systems for loading, unloading, and equipment cleaning.

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* Registered trademark of E.I. Du Pont Co.

9.2 Implementation Profile

Since the current common practice for the disposal of organic waste by incineration is environmentally viable and successfully complies with government standards and regulations, most manufacturers do not have a strong incentive to investigate alternative waste reduction techniques. However, current permit difficulties to site, build and operate an on-site hazardous waste incinerator, combined with increasing land disposal costs and restrictions, could induce source control efforts in those facilities which currently landfill their waste.

9.3 Summary

A summary of the source reduction techniques, along with the associated ratings is given in Table 9-1. The ratings represent the assessment of the relative usefulness among the proposed techniques. It is estimated that the potential waste that could be generated has been reduced to a level characterized by a current reduction index of 2.3 (58 percent). By implementing the proposed source reduction techniques or expanding the use of those already in place, the amount of waste currently being generated can be reduced to a level characterized by a future reduction index of 0.4 to 0.9 (10 to 22 percent). Among the most effective measures are the increase in the recovery of HCl and heating values from the heavy ends and, potentially, control of the quench rate to reduce the byproduct formation.

10. PRODUCT SUBSTITUTION ALTERNATIVES

TCE and PCE have been the principal solvents used for cleaning due to their outstanding ability to dissolve a great variety of oily substances. TCE is used mainly in the vapor degreasing process for metal surface preparation operations. PCE is more widely used in dry-cleaning, textile processing, or cold cleaning of metal surfaces.

TCE can be replaced by other solvents such as 1,1,1-trichloroethane or chlorofluorocarbons (CFC) in metal degreasing operations. In dry-cleaning applications, petroleum-based Stoddard solvent is used as an alternative to PCE. Chlorofluorocarbons, such as 1,1,2-trichloro-1,2,2-trifluoroethane, which are both non-flammable and very low in toxicity, are not used widely mainly due to cost.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE TCE/PCE MANUFACTURING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Heavy Ends (*)	1 Cool reactor effluent gas rapidly	2	1	3	2	2		1.5	0.8	
	2 Control chlorine/hydrocarbon ratio	1	1	2	3	1		1.5	0.1	
	3 Improve fluidization conditions	1	1	1	0	1		0.0	0.3	
	4 Improve catalyst	1	1	2	3	3		1.5	0.4	
	5. Hydrocrack heavy chlor hydrocarbons	1	1	2	0	1		0 0	0.5	
	6. Replace Oxychlorination w/HCl oxid. .	2	2	3	1	1		0 8	0.6	
	7 Oxidize waste w/HCl and heat recovery	3	2	4	2	2		2.0	1.0	1.0
	Overall	1 57	1 29	2 43	1 57	1.57	0.78	2.0	0 5	1 0
Spent Catalyst	1. Use dry dust collectors and filters	1	1	1	0	2		0.0	0.5	0.5
	2. Use of a tougher catalyst support	1	1	3	3	1		2 3	0.2	
	Overall	1.00	1.00	2 00	1 50	1.50	0.01	2.3	0.3	0.5
Spent Caustic Solutions	1 Use NaOH in place of NH3	2	2	2	4	0		2.0	0 0	
	Overall	2 00	2 00	2.00	4.00	0.00	0.10	2 0	0.0	0.0
Drying Waste	1. Use regenerable drying materials	1	1	3	3	1		2.3	0 2	0.2
	Overall	1 00	1.00	3.00	3.00	1.00	0.05	2.3	0.2	0 2
Equipment Cleaning Wastes (*)	1. Increase equipment drainage time	1	1	3	3	2		2.3	0 4	
	2. Lower heat exchanger film temperature	1	1	2	1	1		0.5	0.4	
	3. Electropolish heat exchanger tubes	2	1	3	0	2		0.0	1.5	1.5
	4 Use in-process H.X. cleaning devices	2	1	2	1	2		0.5	0.8	
	Overall	1.50	1.00	2 50	1.25	1 75	0 05	2.3	0.8	1.5
Leaks and Spills	1. Use double mechanical seals on pumps	1	1	3	4	2		3.0	0.0	
	2 Use leak detectors	3	3	2	3	1		1.5	0.1	0.1
	3. Enclosed sampling and analy systems	3	2	2	3	1		1.5	0.1	0.1
	4 Use of vapor recovery systems	2	2	4	4	1		3.9	0.0	
	Overall	2.25	2 00	2.75	3 50	1.25	0 01	3.9	0.1	0.1
All Sources	All Methods						1.00	2.3	0.4	0 9

(*) These waste streams include listed "F" and/or "K" RCRA wastes

Improvement in equipment and techniques which make emission control more effective, may contribute to an increased use of these solvents to replace TCE or PCE in the future. However, it must be noted that since PCE is used as a raw material in the manufacture of several CFCs, their substitution for TCE/PCE may have a limited impact on TCE/PCE production.

Changes in cleaning techniques can be adopted to allow for the use of less powerful cleaning substances in place of TCE and PCE. For example, a combined ultrasonic-alkaline cleaning step would greatly improve the ability of alkaline cleaning solution to remove oily residues, and thus would eliminate the need for using organic solvent cleaners (the reader is also referred to the study of metal parts cleaning contained in this appendix).

The dominant factor controlling the production demand for any solvent (including TCE and PCE) is the extent of the recovery and conservation effort by the users. The increasing costs of waste disposal coupled with tougher and more vigorously enforced air emission standards are likely to result in increased recycling and tighter control of solvent evaporation losses. These, in turn, may lead to the decrease of production demand.

In summary, the likelihood of future decreases in the production rate of TCE/PCE remains strong in view of such factors as the enhanced solvent conservation and recovery efforts by consumers and the availability of less toxic substitutes.

11. CONCLUSIONS

Those TCE/PCE manufacturers who use the oxychlorination route appear to have minimized their waste generation considerably. The reduction is on the order of 60 percent with respect to the waste that would have been produced if none of the noted methods were implemented. Further reductions appear possible, albeit low, on the order of 10 to 20 percent with respect to current waste.

The most effective techniques identified were oxidation of heavy chlorinated waste with attendant HCl recovery and, potentially, control of quench rate to reduce the byproduct formation.

Waste generation from TCE/PCE manufacturing is directly related to the demand for these solvents which, in turn, is influenced by consumer conservation and recycling efforts and substitution of TCE/PCE with other media in cleaning applications.

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13. INDUSTRY CONTACTS

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1. PROCESS: VINYL CHLORIDE MONOMER MANUFACTURE

2. SIC CODE: 2869

3. INDUSTRY DESCRIPTION

Because the manufacture of vinyl chloride involves a capital-intensive process, virtually all of the U.S. vinyl chloride manufacturing capacity is provided by a small number of producers with 14 plant locations (see Table 3-1). Individual plant annual production capacities of major vinyl chloride manufacturers range from 150 million pounds to 1,250 million pounds. In 1984, U.S. plants produced 7,513 million pounds of vinyl chloride (Anonymous 1985a).

Vinyl chloride production units are generally part of large integrated chemical production facilities. Of the 14 major vinyl chloride producing plants, eight are located in Louisiana and four are located in Texas. California and Kentucky each contain one plant.

4. PRODUCTS AND THEIR USE

Most vinyl chloride production is consumed in the manufacture of polyvinyl chloride (PVC) and its copolymers. The small remainder is either exported or used in the manufacture of adhesives and specialty chemicals.

5. RAW MATERIALS

Chemical Feedstocks: ethylene route - ethylene, chlorine, air, or oxygen; acetylene route - acetylene (C_2H_2), hydrogen chloride (HCl).

Drying Agents and Absorbents: silica gel, solid potassium hydroxide (KOH), concentrated sulfuric acid (H_2SO_4), activated charcoal, bauxite, methanol.

Catalysts: $FeCl_3$ (direct chlorination), KCl or $CuCl_2$ (oxychlorination), $HgCl_2$ (acetylene hydrochlorination), on various supports and promoters.

Table 3-1 U.S. Producers of Vinyl Chloride Monomer

Company and Plant Location	Annual Capacity (million pounds)	
Borden Chemical Divison		
Geismar, LA	610	
Dow Chemical U.S.A.		
Freeport, TX	150	
Oyster Creek, TX	750	
Plaquemine, LA	1,250	(a)
Ethyl Corporation		
Baton Rouge, LA	330	(b)
Formosa Plastics Corporation		
Baton Rouge, LA	300	
Georgia-Gulf Corporation		
Plaquemine, LA	1,000	
B.F. Goodrich Company		
Calvert City, KY	1,000	
La Port, TX	1,000	
PPG Industries		
Lake Charles, LA	500	
Shell Chemical Co.		
Deer Park, TX	840	
Norco, LA	700	(b)
Stauffer Chemical Co.		
Carson, CA	174	(b)
Vista Chemicals Company		
Lake Charles, LA	700	
Total	9,304	

Source: Chemical Economics Handbook (SRI 1982); PPG Industries 1985: Personal communication.

(a) Source at Dow Chemicals indicates that capacity is lower.

(b) Plant not operating at present.

6. PROCESS DESCRIPTION

Detailed process descriptions for vinyl chloride monomer (VCM) production have been presented in open literature (Cowfer and Magistro 1983, McPherson, Starks, and Fryar 1979, Sittig 1978, Liepins et al. 1977). The following paragraphs are based on a review of the literature and on industry comments. The two main methods of production of vinyl chloride, the acetylene route and the ethylene route, are discussed. The descriptions presented below are general and may not account for all different configurations encountered in the actual plant design.

Prior to the 1950's, the acetylene process for the manufacture of VCM was dominant. As ethylene became plentiful and the demand for VCM increased, the commercial processes shifted to the ethylene route. Currently, most of VCM production in the U.S. is from ethylene. The acetylene route is still practiced only in one installation owned by Borden Chemicals.

In the first route, the acetylene feed is reacted with HCl. The acetylene feed is first dried by passing it through a bed containing silica gel, KOH solid or concentrated H_2SO_4. The HCl feed is dried by contacting it with concentrated H_2SO_4. The dehydrated feed streams are mixed in a chamber containing activated charcoal to adsorb small quantities of Cl_2 present in HCl; this is done to prevent explosive chloroacetylene formation. The drying agents and activated carbon are periodically regenerated and discarded eventually as wastes.

The mixture is then passed through packed tubes containing mercuric chloride on activated charcoal as a catalyst. Thorium, cerium, cadmium, and/or potassium chlorides are used in conjunction with mercuric chloride. The products are vinyl chloride, ethylidene chloride, acetaldehyde, unreacted HCl and C_2H_2. The spent catalyst containing mercuric chloride is a potentially hazardous waste stream. The inorganic impurities from the product are removed by alkaline and water scrubbing. Water is removed by freezing the scrubbed gas stream or passing it through a methanol column or a bauxite drier. Secondary drying of VCM is accomplished by contact with solid KOH. The first distillation column removes low molecular weight gaseous impurities at low pressure. In the second column VCM is further purified. Yields as high as 99 percent are possible.

The more predominant ethylene route, shown schematically in the block flow diagram in Figure 6-1, consists of 3 basic reaction steps:

1. Direct chlorination of ethylene to ethylene dichloride (EDC):
   $CH_2 = CH_2 + Cl_2 \longrightarrow CH_2Cl - CH_2Cl$

2. Oxychlorination of ethylene to EDC using HCl and O_2:
   $CH_2 = CH_2 + 2HCl + \frac{1}{2} O_2 \longrightarrow CH_2Cl - CH_2Cl + H_2O$

3. Pyrolysis of EDC to VCM and HCl:
   $2\ CH_2Cl - CH_2\ Cl \xrightarrow{heat} 2CH_2 = CHCl + 2\ HCl$

Direct chlorination is conducted by passing ethylene and chlorine gas through liquid EDC at 80-250°F (depending on whether a sub-cooled or boiling reactor is used) and at pressures close to atmospheric or higher. The reaction is homogeneously catalyzed by ferric chloride dissolved in EDC. The heat of reaction is dissipated either by cooling with water coils or by the vaporization of EDC, with the reactor operating at the boiling point.

EDC is produced at very high yield and can be withdrawn either as a liquid (sub-cooled reactor) or as a vapor (boiling reactor). Where liquid withdrawal is used, $FeCl_3$ must be removed from EDC using an acid wash, or by adsorption on a solid such as activated carbon. With vapor withdrawal, no $FeCl_3$ separation step is necessary.

Oxychlorination also produces EDC for use in pyrolysis, except that it uses HCl recycled from the pyrolysis step, thus resulting in zero net HCl production from the entire process. This was precisely the reason why oxychlorination was added to the direct ethylene chlorination step in the 1950's, when HCl produced by the direct chlorination and pyrolysis steps could not be marketed. Oxychlorination is typically conducted at 430-490°F and 20-270 psig in fluid bed reactors, or at 450-570°F and 20-200 psig in tubular fixed bed reactors in the presence of cupric chloride catalysts. Temperature control of this highly exothermic reaction is of paramount importance to waste generation, as temperatures in excess of 620°F result in an increased byproduct formation. Other penalties for excessive temperatures include catalyst deactivation and loss of ethylene through burning.

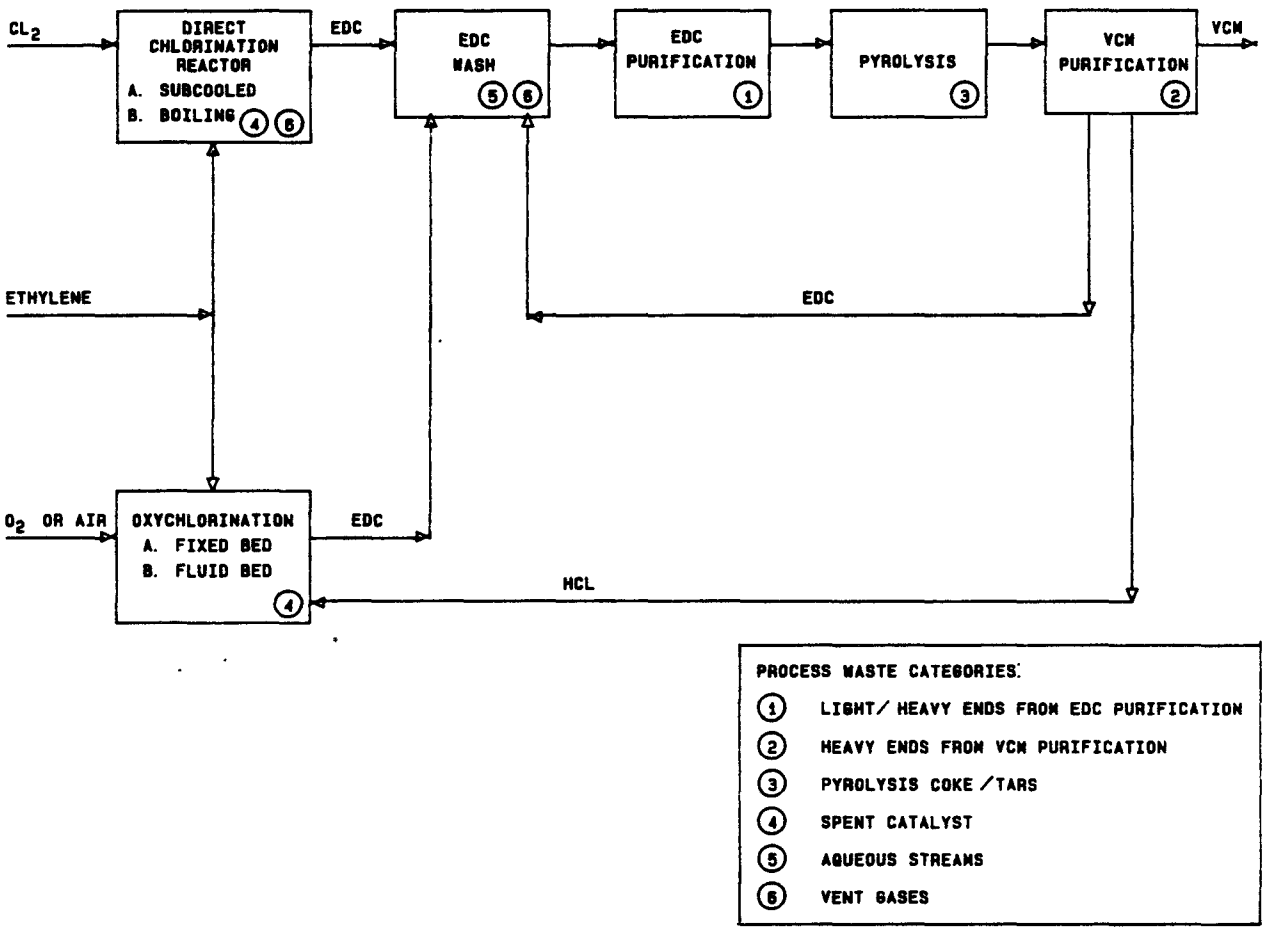

Figure 6-1 Vinyl Chloride Manufacture via Ethylene Route

The excellent temperature control characteristics of fluid beds led to the development of the fluid bed reactor, which successfully competed with the older fixed bed tubular design. Fluid beds offered improved EDC yield over the fixed bed reactor. In recent years, however, the introduction of new catalysts increased the yields and made the fixed bed reactor technology more competitive with the fluid bed reactors.

Either air or oxygen can be used in oxychlorination; however, the trend has been toward use of oxygen which drastically reduces vent gas volume and associated losses. The hot oxychlorination reactor effluent gas is condensed and the condensate containing EDC and water is sent to the EDC treating and purification section. The offgas is treated with chlorine to convert unreacted ethylene to EDC, which then is removed through solvent absorption or refrigerated condenser. For the oxygen-blown reactor, it is possible for excess ethylene to be recycled back to the oxychlorination unit.

Comparison between direct chlorination and oxychlorination shows that the latter produces more impurities. These include ethyl chloride, vinylidene chloride, 1,1-dichloroethane, chloral and others. EDC from direct chlorination, oxychlorination and pyrolysis (after treatment) is washed with water and caustic to remove water soluble impurities (e.g., chloral), and then distilled in two steps to yield 98-99.9 percent pure EDC for pyrolysis. Distillation also yields light and heavy end waste streams.

The endothermic pyrolysis step is conducted at 900-1025°F and usually in the 50-500 psig pressure range. After pyrolysis, the products are rapidly quenched to avoid increased heavy ends and tars formation. HCl is recycled back to the oxychlorination section. The VCM product is then separated from the unreacted EDC via distillation and EDC is recycled back to the purification section, usually following chlorination to convert chloroprene and trichloroethylene. The pyrolysis step produces a large portion of byproducts, most of which are removed when unconverted EDC is washed and distilled in the EDC purification/treatment section ahead of pyrolysis.

7. WASTE DESCRIPTION

The primary wastes associated with VCM production are shown in Table 7-1. The wastes consist of liquid, solid, and gaseous streams and, when economically feasible, are processed on-site to recover some of the chemicals. In highly integrated

Table 7-1. Process Wastes from VCM Manufacturing Process

No.	Waste Description	Process Origin	RCRA Codes
1	Light and heavy ends from EDC purification	Direct chlorination reactor Oxychlorination reactor Pyrolysis reactor	K019*
2	Heavy ends from VCM purification	Pyrolysis reactor	K020
3	Pyrolysis coke/tars	Pyrolysis reactor	K024
4	Spent catalyst	Direct chlorination ($FeCl_3$) Oxychlorination	---
5	Aqueous streams	Oxychlorination water EDC wash solutions	---
6	Vent streams	Misc. equipment	---
7	Leaks & spills	Misc. equipment & piping	---
8	Equipment cleaning	Tanks, towers, heat exchangers, piping	F024

* RCRA code covers heavy ends only.

manufacturing facilities, some of these streams are used as feedstocks to other manufacturing units, and hence are not classified as "wastes". The wastes shown in Table 7-1 can be further grouped into the following categories.

Organic Liquid Wastes

The EDC purification step yields light and heavy ends chlorinated hydrocarbons which are removed in two consecutive distillation steps prior to pyrolysis. Both streams undergo reprocessing in many facilities in the following ways (USC 1983):

- High efficiency thermal oxidation followed by water or caustic scrubbing of the flue gas (SCC 1981). This process may be preceded by an additional distillation step to effect further recovery of useful chemicals.

- Catalytic oxidation with heat recovery and direct recycle of HCl-bearing flue gas to oxychlorination (Benson 1979).

- Chlorination at elevated temperature and pressure. The process ultimately yields carbon tetrachloride and/or perchloroethylene.

Other disposal methods include landfilling, deep well injection and at-sea incineration, which is currently practiced on a developmental basis (Benson 1979, Scharein 1981). Land disposal is practiced only by a few manufacturers; others use the recycling techniques mentioned above. Ocean dumping was discontinued in the United States.

Crude VCM is purified, yielding a bottoms stream which contains heavy ends from the pyrolysis section. In an integrated plant, VCM heavies can be routed to the EDC still; in non-integrated plants, they are stripped of EDC which is recycled to pyrolysis. Ultimately, this stream is expected to be disposed of by incineration, landfill or subjected to further chlorination to yield other chlorinated organic products.

Solid Wastes

Pyrolysis tars and coke form as a result of thermal reactions inside the tubes of the cracking (pyrolysis) furnace and are periodically removed to restore heat transfer and to lower the hydraulic resistance of the equipment. The solids can be either incinerated or landfilled.

Spent catalyst waste stream is comprised of $FeCl_3$ catalyst from the direct chlorination section and spent $CuCl_2$-based catalyst from the oxychlorination section. In direct chlorination, the subcooled reactor generates a considerably larger $FeCl_3$ stream compared to the boiling reactor, owing to the withdrawal and subsequent wash of the liquid EDC stream containing dissolved catalyst (by comparison, the boiling reactor generates a vapor EDC stream with virtually all $FeCl_3$ left behind).

In oxychlorination, the catalyst is $CuCl_2$ on various supports (e.g., alumina or silica-alumina). The catalyst waste is generated due to deactivation and due to attrition (in the fluidized beds only).

Aqueous Wastes

Aqueous streams originate from various EDC washing and vent scrubbing operations involving alkaline solutions and from the formation of water in the oxychlorination reaction. The wastewater is typically steam-stripped to remove volatile organics, neutralized and treated in an activated sludge system prior to discharge.

Vent Streams

Vent streams originate mainly from the non-condensibles present in the offgas from the direct chlorination and oxychlorination. The air-blown process generates a considerable vent stream. The treatment includes high efficiency incineration or catalytic combustion and scrubbing with alkaline solutions.

Spills & Leaks

Leaks and spills along with equipment cleanup are minor effluents in comparison with the waste streams mentioned above. Due to the highly toxic nature of process fluids and the resulting regulation of emissions, the quantity of leaks and spills from the VCM process has been greatly reduced in the last ten years.

Equipment Cleaning Wastes

The equipment cleaning wastes include periodic wastestreams originating from the steamout of process vessels and the chemical or mechanical cleaning of heat exchangers and piping. These do not include pyrolysis coke and tars from the cracking

furnace, which were considered separately. Disposal methods for equipment cleaning wastes probably vary from facility to facility and it is likely that land disposal is practiced.

8. WASTE GENERATION RATES

The current waste generation rates were not in evidence at the time of the final document preparation. The 1974 specific waste generation rates found (Liepins et. al. 1977, USEPA 1975); however, according to industry contacts these rates have undergone a substantial decrease and are outdated.

The approach used to estimate the achieved and projected reductions in waste generation requires that relative (or fractional) waste generation rates be known. Such were compiled by the project staff using information obtained from the industry and are shown in Table 8-1.

Table 8-1 Waste Generation Profile for the Vinyl Chloride Industry

Waste/ Residual	Total Percent (by weight)
Organic Liquids	10
Spent Catalyst	1
Solids	1
Aqueous Streams	87
Leaks and Spills	1
Equipment Cleaning	1
Total	100

Source: Estimated by project staff

9. SOURCE REDUCTION TECHNIQUES

9.1 Description of Techniques

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" have also been included. Good operating practices are defined as

being procedural or institutional changes which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel practices
  - management initiatives
  - employee training
- o Procedural measures
  - documentation
  - material handling and storage
  - material tracking and inventory control
  - scheduling
- o Loss prevention practices
  - spill prevention
  - prevention maintenance
  - emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified. The primary waste streams and their source reduction methods are summarized in Table 9-1. The following is a description of the source control techniques considered for each of the waste sources.

9.1.1 Liquid Organic Wastes

As mentioned previously, these wastes are composed of distillation light and heavy ends separated out during EDC and VCM purification processes in separate distillation steps. At highly integrated manufacturing facilities, these streams are often used as feedstocks to other units and, as such, are not classified as wastes. The primary process origins of liquid organic waste include oxychlorination and pyrolysis reactors. Direct chlorination is not a significant byproduct generator, as catalyst selectivity is excellent. Sections below describe source control methods that have actual or potential application to reduce byproduct formation.

9.1.1.1 Oxychlorination Step

Minimization of waste generation from the oxychlorination step could conceptually be approached in two ways. First, improvements to the oxychlorination process could be made to reduce the formation of the undesirable byproducts. Second, the oxychlorination step can be avoided altogether by replacing it with an alternative low-waste process. Byproduct generation is related to the following five main aspects of the oxychlorination reaction: temperature uniformity and control, feed purity, use of oxygen versus air, catalytic selectivity, and gas-catalyst contact.

The following practiced and proposed source reduction methods have been identified:

- Use of fluidized bed reactors as opposed to fixed bed reactors.
  Fluid bed reactors are characterized by better temperature uniformity and lower operating pressures and temperatures in comparison to fixed bed designs. Fluidized bed reactors are more widely used than older fixed bed designs (Leddy et al. 1983). However, recent improvements in the catalyst performance make the fixed bed technology competitive again with the fluid bed designs.

- Modifications to tubular fixed bed reactor design.
  Currently practiced modifications include: an increase in catalyst concentration along the reaction path to avoid hot spotting; minimization of radial temperature gradient by optimizing tube diameter; and staging of consecutive oxygen or air injection.

- Use of oxygen instead of air.
  This decreases EDC vent losses and byproduct formation. The EDC obtained from the O_2-based oxychlorination can be comparable in purity to EDC obtained from direct chlorination*. The manufacturers have been shifting to the oxygen-based process for oxychlorination because of product purity and lower vent gas loads (Leddy et al. 1983). The opinions on whether the O_2-based process is economically advantageous over the air-based process are split.

- Selective hydrogenation of acetylene in the feed.
  This has been practiced to reduce subsequent byproduct formation in the oxychlorination reactor (Leddy et al. 1983).

- Use of improved catalysts.
  The efforts to improve the selectivity, stability and attrition resistance of oxychlorination catalysts yielded improvements, especially for the fixed bed applications. New fixed bed catalysts offer significant lifetime improvements; one catalyst offered by a Japanese manufacturer since 1983 can extend the lifetime from 9 to 18 months*.

- Re-examination of reactor conditions.
  Additional means of improving the oxychlorination process to reduce byproduct formation can be postulated. These include: a thorough investigation of the effects of reducing the effective bubble size in fluid beds (e.g., using shorter pitch of the cooling coil bundle) to promote gas-catalyst contact; variations of the ethylene recycle rate; a decrease in operating pressure; and quick post-reactive cooling.

The identified alternatives to oxychlorination include an HCl oxidation step, the use of an ethylene/acetylene route, and the use of the Akzo-Zout Chemie process.

- Replacement of oxychlorination with an HCl oxidation step.
  In this scheme, the formation of the undesirable byproducts due to oxychlorination is avoided by oxidation of the purified pyrolysis HCl and subsequent Cl_2 recycle back to the direct chlorination EDC production unit (see Figure 9-1).

  HCl oxidation can be accomplished in one of two ways:

  - Direct oxidation (Schreiner et al. 1974, Bostwick 1976)

    $$2HCl+\tfrac{1}{2}O_2 \longrightarrow Cl_2+H_2O$$

  - Electrolytic oxidation (Payer 1974)

    $$2HCl \longrightarrow H_2+Cl_2$$

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* Conoco Inc. 1986: Private communication.

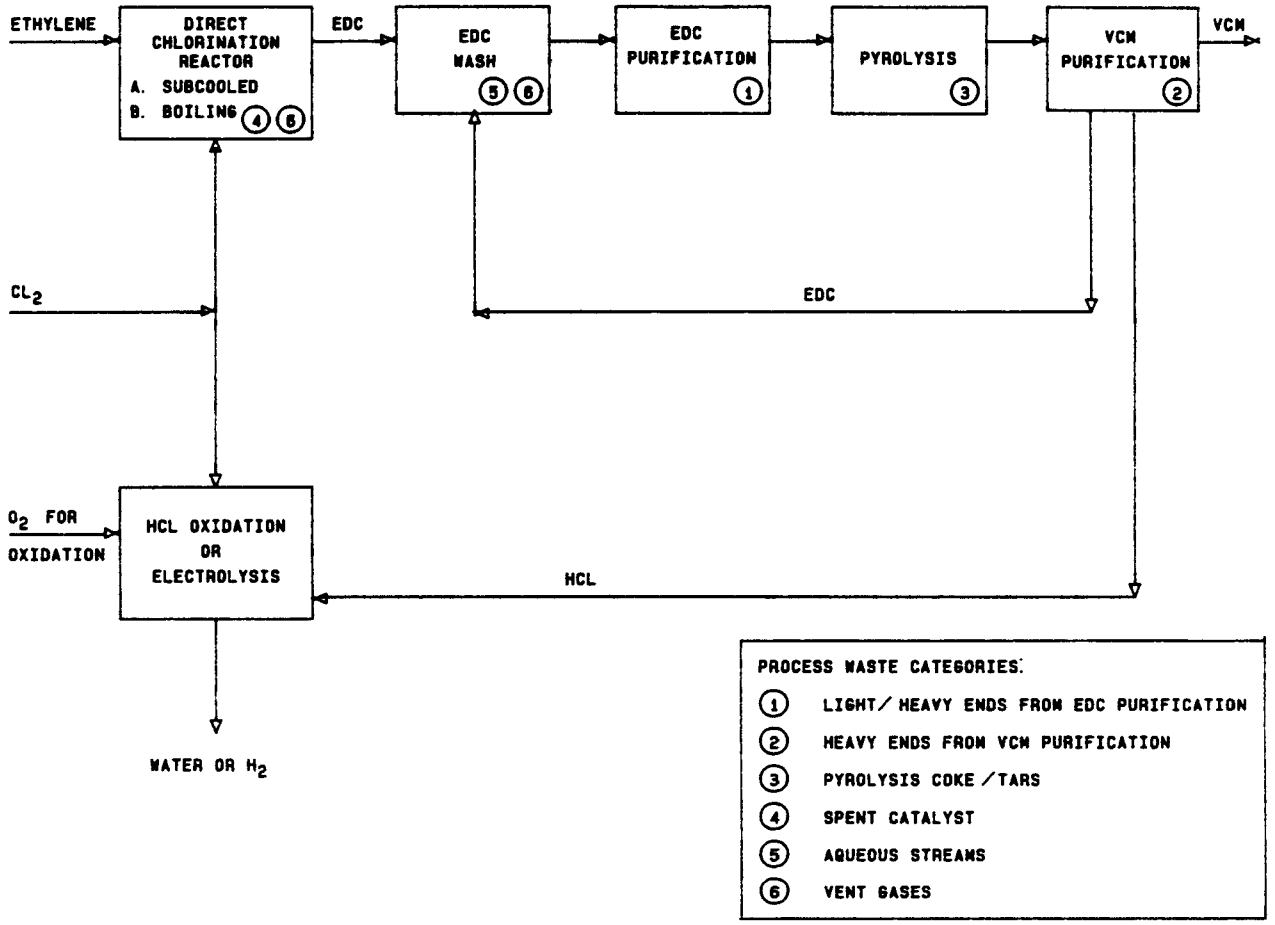

Figure 9-1 Vinyl Chloride Manufacture via an Alternate Process Scheme with HCL Oxidation Replacing Oxychlorination

Both schemes employ commercially proven processes such as the Deacon, Shell, or Kel-Chlor process for direct oxidation, or the Westvaco or Bayer-Hoechst-Uhde process for electrolytic oxidation (Leddy et al. 1983, Versar 1979). Shell Oil operates a 19,000 TPY pilot plant at Pernis in the Netherlands using a modified Deacon process for direct oxidation (Versar 1979). Du Pont operates a 200,000 TPY plant at Corpus Christi, Texas using the Kel-Chlor process (Versar 1979). The Hoechst-Uhde process is practiced at 14 plants in various countries with a total capacity of 1400 tons per day using electrolytic oxidation*. Mobil Chemical has operated two electrolytic HCl oxidation units in their toluene diisocyanate facility in Baytown, Texas.

The postulated advantages of the HCl oxidation route over the currently used oxychlorination route include:

- Waste byproducts of oxychlorination are totally avoided; instead, a high-quality EDC stream from direct chlorination can be further purified at minimum expense.

- Purer EDC feed to pyrolysis results in a decreased waste byproduct generation during the pyrolysis step.

- Waste water is produced outside of the organic phase, thus avoiding costly waste treatment and the disposal of ultimate treatment residuals associated with organics carryover.

- Reaction water generation can be largely avoided in an electrolytic step.

The principal disadvantages are the current high capital and operating costs. Numerous examinations of the HCl oxidation processes indicate that they were not economically competitive with oxychlorination*. Excessive costs are the reason for the planned shutdown of the only U.S. installation of the direct HCl oxidation process

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* Hoechst-Uhde Corporations 1986: private communication.

** Dow Chemical Company 1985: Personal communication; PPG Industries 1985: Personal communication.

(Kel-Chlor) at Du Pont's Corpus Christi facility*. The economics of these processes was discussed in detail (Versar 1979). The Kel-Chlor process is economical only for large scale units (600-1000 TPD of HCl loads) using the oxygen-based process. The high capital cost of the Kel-Chlor process is partly due to the tantalum construction required because of the corrosive process environment. The Hoechst-Uhde process, though suitable for any capacity due to modular construction of electrolysis units, may not be economically competitive with oxychlorination even though the electricity requirements were reduced from 1900 kWh per metric ton of Cl_2 in 1964 to 1400 kWh presently. Further reductions in electricity consumption can be explored in the area of H_2 fuel cell technology. Even if the HCl oxidation alternative is viable for a grass roots plant, it may not be affordable to existing plants which are currently handling their wastewaters in an environmentally acceptable manner.

- Mixed feedstock option.

  Another process option is the use of a mixed feedstock of ethylene and acetylene (Cowfer and Magistro 1983). HCl produced in the pyrolysis step can be reacted with acetylene to produce VCM, thus avoiding oxychlorination of ethylene. The mixed feed stock option depends on economic and geographic conditions, and the development of lower cost routes to the production of acetylene. At the present, acetylene routes generally lack economic feasibility. The environmental disadvantage of this process is the generation of spent catalyst (mercuric chloride on activated carbon) which is potentially hazardous.

- Akzo-Zout Chemie process.

  An alternate route to VCM, which is still in its experimental stages, converts ethylene, sodium chloride, oxygen, and carbon dioxide to EDC and sodium bicarbonate (Anonymous 1983). EDC can then be pyrolyzed to yield VCM, and sodium bicarbonate can be calcined to soda ash. This route eliminates the direct chlorination and oxychlorination routes to produce VCM. This process is being patented by Huls (Germany) and Akzo-Zout

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* Du Pont 1986: Personal communication.

Chemie B.V. (Hengelo, the Netherlands). The process uses a homogeneous catalyst of complexed ions of trimethylamine hydrochloride, copper chloride and iodine in adiponitrile solvent. The development work on this process was halted*. The advantages and disadvantages of the process over the conventional routes from a waste minimization point of view could not be assessed due to the lack of available data.

9.1.1.2 Pyrolysis Step

Generation of byproducts from the pyrolysis reaction has been an area of considerable investigative effort. The following is a listing of both practiced and postulated techniques for reducing byproduct formation:

- o A laser-induced EDC cracking technique.
  Under development by the Max Planck Institute in West Germany, laser-induced EDC cracking is claimed to have a considerably lower byproduct yield than thermal cracking (Wolfrom 1979, 1980). At the present, the process is not a commercially proven technology; the problem of the availability of a large size laser still persists.

- o Use of additives to EDC feed.
  Additives such as chlorine or carbon tetrachloride, have been reported in patent literature to suppress methyl chloride formation (Cowfer and Magistro 1983). According to Dow Chemical, methyl chloride is only a minor impurity (less than 40 ppm in VCM). The presence of nitromethane was reported to increase EDC conversion to 92.5 percent (McPherson, Starks and Fryar 1979).

- o More stringent control of EDC feed purity.
  This widely practiced technique reduces fouling and byproduct formation during pyrolysis.

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* Vinyl Chloride Institute 1985: Personal communication.

- Rapid quench rate.
  Byproduct formation depends to a large measure on how quickly the pyrolysis offgas is cooled. If cooling is done too slowly, the VCM yield is substantially decreased with attendant formation of undesirable byproduct. The technique of direct quench of the hot pyrolysis offgas using cold recycled EDC condensate is widely practiced.

9.1.2 Solid Wastes

Solid wastes from the manufacture of VCM consist of pyrolysis tars and coke produced in the cracking furnace, spent catalysts, catalyst fines from oxychlorination, and spent drying reactants. Possible measures to reduce these wastes are:

- Modification and/or proper control of the pyrolysis process.
  Coking can be reduced through a reduction of the trichloroethylene concentration in the feed to the cracking furnace (opinions are split on this issue*), temperature profile monitoring along the pyrolysis path, and the use of an alternate laser-induced EDC cracking process (Wolfrom 1979, 1980). Of these measures, only temperature monitoring appears to have the largest immediate utility for further application.

- Convert pyrolysis tars into valuable byproducts.
  Chlorinated tars and coke can be blended with other chlorocarbon streams and treated in a combination of thin-film evaporators and decomposition screws to produce HCl, carbon black (low in chlorine), and some useful low boiling chlorohydrocarbons. This process is in commercial operation at Chemische Werke Huls AG, West Germany (Scharein 1981).

- Reduction of the oxychlorination catalyst attrition rate.
  The oxychlorination catalyst fines generation rate can be decreased by reducing the attrition rate through use of a more stable catalyst support. Catalyst attrition can largely be avoided by using fixed bed reactors, though they may suffer from temperature maldistribution (hot-spotting) problems.

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* Vinyl Chloride Institute 1985: Personal communication.

- o Prevention of oxychlorination catalyst deactivation.
  Excessive temperatures result in volatilization and subsequent loss of $CuCl_2$ from the catalyst leading to its deactivation. Avoidance of upsets resulting in excessive temperature episodes will contribute to curtailment of the catalyst loss and the associated generation of waste. Also, as discussed previously, new fixed bed catalysts offer significant lifetime improvement over older ones.

9.1.3 Aqueous Wastes

Process related aqueous waste streams originate mainly from:

- Water produced in oxychlorination.
- Miscellaneous washing operations.

Oxychlorination water is a necessary reaction product and cannot be avoided without drastic revamping of the entire process scheme. A process option where water is produced outside of the organic phase--or is not produced at all--is to substitute the oxychlorination step with an HCl oxidation step as discussed before. In concept, the elimination of oxychlorination water formation by electrolytic HCl oxidation is possible, but the attendant reduction in the hazardous waste loads attributable to water will probably be very small (possibly through avoidance of organics carryover into wastewater treatment and an associated reduction of the treatment sludge volume).

Other sources of wastewater are washing operations to remove water-soluble impurities. Washing operations are performed on EDC to remove $FeCl_3$ when using a subcooled reactor for direct chlorination and on EDC from oxychlorination, to remove water soluble impurities (mainly chloral). The washing operations are often performed on combined EDC feed to the pyrolysis section prior to distillation and drying. Water use and the associated treatment waste can be minimized by the following practiced source reduction techniques:

- o Use of solid absorbent for $FeCl_3$ catalyst removal from EDC liquid effluent from the direct chlorination reactor.

- Use of boiling vs. subcooled reactors.
  As explained in sections 6 and 7, the boiling reactor for direct chlorination produces EDC in vapor form, thus obviating the need for continuous $FeCl_3$ removal in large quantities from the effluent. The original catalyst charge is replaced much less frequently by comparison to the subcooled reactor design.

  Boiling reactors, pioneered by Stauffer Chemical Company, are already in widespread use. Boiling reactors eliminate the need to wash $FeCl_3$ out of the EDC produced and thus eliminate the generation of related treatment residuals (McNaughton 1983). Also, steam consumption is drastically reduced, which results in limiting the boiler feedwater treatment wastes.

- Use of multi-stage countercurrent contactor for EDC pyrolysis feed washing. When washing is to be performed, a multi-stage countercurrent contactor will produce a smaller, more concentrated wash-water stream than will a single stage.

9.1.4 Spills and Leaks

Due to the toxic/carcinogenic nature of VCM, a great deal of attention has been paid to reducing fugitive emissions from VCM plants. In 1974, EPA estimated that a typical VCM plant lost through leakage 0.1215 kg of VCM per 100 kg of VCM produced. The EPA formulated various regulations to reduce these emissions by 94 percent. Since 1974, the VCM industry has reduced leakage by a factor of ten*. The following source reduction techniques are considered as good operating practices, with many being actually mandated by the 1976 VCM standards (NESHAP 1984):

- Replace single mechanical seals with double mechanical seals on pumps or use canned seal-less pumps.

- Use of bellows sealed valves to limit leakage around stem packing.

- Use of leak detection systems and portable monitors.

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* Dow Chemical Co. 1985: Personal communication.

- o Enclosed sampling and analytical systems.

- o Use of vapor-recovery systems for VC loading, unloading and equipment cleaning.

9.1.5 Equipment Cleaning Wastes

Generation of this minor waste stream can be minimized by:

- o More complete drainage of process piping or equipment prior to cleaning.

- o Lower process film temperatures and higher turbulence at the heat exchange surfaces to reduce fouling rates.

- o Use of non-stick (electropolished or Teflon*) heat exchanger tubes to reduce deposit clingage (Anonymous 1985c).

- o Use of in-process heat exchanger tube cleaning devices (Anonymous 1985b).

All the suggestions listed above will have only a minor impact on overall waste generation, since equipment cleaning wastes are but a small fraction of the total waste.

9.2 Implementation Profile

VCM plants tend to be an integral part of large chlorohydrocarbon production facilities where significant capital has been invested to handle process wastes and effluents in an environmentally acceptable manner. This makes waste minimization infeasible, unless significant economic benefits can be demonstrated. In this context, a basic process modification requiring substantial capital investment would need extensive economic evaluation, including consideration of the incremental profit due to the increased VCM yield, the incremental decrease in waste treatment and disposal costs, and the avoidance of future costs associated with liability for environmental impairment.

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* Registered trademark of E.I. Du Pont de Nemours Co.

Most waste minimization measures identified in this work are capital-intensive, hence their implementation appears more likely for the grass-roots plants than for the existing ones. Other measures identified in this report are still developmental in nature (laser-induced pyrolysis, mixed feed operation, or Akzo-Zout Chemie process), lack economic feasibility at their current stage of development (HCl oxidation route), or would have only a relatively small impact (use of non-stick heat exchanger surfaces).

9.3 Summary

The summary of all noted source control techniques is given in Table 9-1. Each technique was rated for its effectiveness, extent of current use and future application potential on scale of 0 to 4. The ratings were derived by project staff based on review of the available data and in consultation with the industry. The estimates of current level of waste reduction achieved (current reduction index) and possible future reduction (future reduction index) were obtained from the ratings in accordance with the methodology presented in the introduction to this appendix.

The current reduction index (CRI) is a measure of reduction of waste that would be generated if none of the methods listed were implemented to their current level of application. For the entire VCM process, CRI is 1.5 (38 percent) which is indicative of the moderate level of waste minimization that already has taken place. It must be noted, however, that reduction of waste was not a primary objective behind most of these measures; rather, it was the effort to increase VCM yield or energy efficiency of the process.

The future reduction index (FRI) is an indication of the level to which the currently generated waste can be reduced if all of the techniques noted were implemented according to their rated potential. The FRI value of 0.1 to 0.3 (2 to 8 percent) is indicative of low extent of future waste reductions. Among the techniques that were found currently most effective and applicable (as evidenced by high FRI value) for control of liquid organic wastes was selective hydrogenation of C_2H_2 in the feed, use of improved catalysts and fluid beds in oxychlorination, and use of additives to the EDC feed to pyrolysis. Use of boiling reactors for direct chlorination was found effective in reduction of solid waste ($FeCl_3$ catalyst), washwater and water treatment sludges.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE VINYL CHLORIDE MONOMER MANUFACTURING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Liquid Organics Oxychlorination Reactor (*)	1 Use fluid-bed over fixed bed reactor	3	3	2	2	1		1 0	0.3	
	2. Modify fixed bed reactor design	1	1	2	3	1		1.5	0.1	
	3. Use oxygen instead of air	3	3	1	3	1		0 8	0.1	
	4. Selective hydrogenation, C2H2 in feed	1	1	4	3	3		3 0	0.8	0 8
	5 Use improved catalysts	1	1	1	2	2		0 5	0.3	
	6. Re-examine reaction conditions	1	1	2	3	1		1.5	0.1	
	7 Replace Oxychlorination w/HCl oxid.	2	3	4	0	0		0.0	0 0	
	8. Use mixed C2H4/C2H2 feed option	1	1	1	1	1		0 3	0.2	
	9. Use Akzo-Zout Chemie process	1	2	0	0	0		0.0	0 0	
	Overall	1.56	1.78	1 89	1 89	1 11	0.05	3.0	0.2	0.8
Liquid Organics Pyrolysis Reactor (*)	1. Use of laser induced pyrolysis	2	2	2	0	0		0.0	0.0	
	2. Use of additive to EDC pyrolysis feed	1	1	1	2	2		0.5	0 3	0.3
	3. Tighter control of EDC purity	1	1	2	3	1		1 5	0 1	
	4. Quench products rapidly	1	1	3	4	0		3.0	0.0	
	Overall	1.25	1.25	2.00	2.25	0 75	0 05	3.0	0.1	0.3
Solid Waste Pyrolysis Coke and Tars (*)	1. Proper control of pyrolysis	1	1	2	3	1		1.5	0.1	
	2 Recover products from solid waste	3	3	3	0	1		0 0	0.8	0 8
	Overall	2.00	2.00	2.50	1.50	1.00	0.01	1 5	0.4	0.8
Solid Waste Spent Catalysts	1. Reduce oxychlor cat attrition rate	1	1	2	3	1		1.5	0.1	
	2. Prevent catalyst deactivation	1	1	1	3	1		0 8	0 1	
	3. Use boiling versus sub-cooled reactor	2	3	3	3	2		2.3	0.4	0 4
	Overall	1.33	1.67	2 00	3 00	1.33	0.01	2.3	0.2	0.4
Aqueous Waste Oxychlorination	1 Use electrolytic HCl oxid vs oxychlor	2	2	3	0	0		0.0	0.0	
	Overall	2.00	2 00	3 00	0 00	0 00	0 60	0.0	0.0	0.0
Aqueous Waste EDC Washing	1. Use solid FeCl3 absorbent	1	1	1	0	1		0.0	0 3	
	2 Use boiling versus sub-cooled reactor	2	3	2	2	3		1.0	0 8	0.8
	3. Use multistage countercurrent wash	1	1	2	4	0		2.0	0.0	
	Overall	1.33	1.67	1.67	2.00	1.33	0.26	2 0	0.3	0.8
Spills and Leaks	1. Use double mechanical seals on pumps	1	1	3	3	3		2 3	0.6	0.6
	2. Use bellows seal valves	3	3	2	1	1		0 5	0.4	
	3. Use leak detectors and monitors	3	3	0	3	3		0.0	0.0	
	4. Enclosed sampling and analy. systems	3	2	3	3	3		2 3	0 6	0.6
	5 Use of vapor recovery systems	2	2	0	4	4		0 0	0.0	
	Overall	2.40	2 20	1 60	2.80	2 80	0.01	2 3	0 3	0.6
Equipment Cleaning Wastes (*)	1 Increase equipment drainage time	1	1	2	3	4		1.5	0.5	
	2 Electropolish heat exchanger tubes	2	1	2	0	2		0 0	1.0	1.0
	3 Lower heat exchange film temperature	1	1	1	3	1		0 8	0.1	
	Overall	1 33	1 00	1 67	2 00	2 33	0.01	1.5	0 5	1 0
All Sources	All Methods						1 00	1.5	0 1	0 3

(*) These waste streams include listed "F" and/or "K" RCRA wastes.

Among the techniques that were found potentially most effective were the use of electrolytic HCl oxidation in place of oxychlorination and the use of laser-induced pyrolysis. Both will probably require substantial development effort before both economic and technical feasibility are fully established.

10. PRODUCT SUBSTITUTION ALTERNATIVES

Since most VCM output is consumed by PVC production, the principal product substitution routes must be explored primarily in the area of PVC applications. Long-term demand for PVC is expected to remain stable, although in the short term the operating capacity has steadily been decreasing. In 1981, about 50 percent of PVC was consumed in construction-related uses (SRI 1982). Clay, cast iron, or ductile steel can replace PVC in piping uses. This substitution is economical only for pipe diameters larger than 16 inches. Aluminum is an effective substitute for PVC in the irrigation pipe market.

Other PVC uses include consumer goods, electrical, and packaging uses. Product substitution in these areas, even if possible, would have only a minor impact on the total PVC demand.

11. CONCLUSIONS

While the VCM manufacturing industry appears to have appreciably minimized their waste (current reduction index of 1.5), it is also apparent that very modest further reductions are possible (future reduction index of 0.1 to 0.3). The most effective control methods appear to be selective hydrogenation of acetylene in the ethylene feed to oxychlorination, use of fluid bed reactors and improved catalyst in oxychlorination, use of additives to the EDC feed to pyrolysis and use of boiling reactors.

The technical and economic details of replacing oxychlorination with direct or electrolytic HCl oxidation appear to be worth exploring, since the measure would be very effective in eliminating the organic liquid wastes from oxychlorination. The currently prohibitive economics of the HCl oxidation route is a problem; however, the potential benefits may justify the search for cost-effective solutions. Laser-induced pyrolysis, while in the developmental stage, offers a substantial potential for reduction in pyrolysis byproduct formation.

The identified PVC product substitution alternatives include clay, cast iron, steel or aluminum piping.

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13. INDUSTRY CONTACTS

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1. PROCESS: WOOD PRESERVING
2. SIC CODE: 2491
3. INDUSTRY DESCRIPTION

As defined in Standard Industrial Classification (SIC) 2491, the wood preserving industry "comprises establishments primarily engaged in treating wood, sawed or planed in other establishments, with creosote or other preservatives to prevent decay and to protect against fire and insects. This industry also includes the cutting, treating, and selling of crossties, poles, posts, and piling."

3.1 Company Size Distribution

Of the 524 wood preserving facilities located in the U.S., 65 percent employ less than twenty people each (USDC 1985). Overall, the Bureau of the Census estimated that 10,900 people were employed by the wood preserving industry in 1982. Table 3-1 lists company size distribution as a function of total number of employees per facility.

Table 3-1 1982 Company Size Distribution

	No. of employees per facility				
	Total	1-19	20-49	50-99	100+
No. of facilities	524	340	131	40	13
No. of employees	10,900	2,400	4,200	2,800	1,500

Source: 1982 Census of Manufacturers (USDC 1985).

3.2 Principal Producers

The wood preserving industry is composed of a small percentage of multi-plant firms and a large number of single plant firms. The six major wood preserving companies in the U.S. are:

Koppers Co., Inc.
Kerr McGee Chemical Corp.
Southern Wood Piedmont Co.
J.H. Baxter & Co.
Wyckoff Co.
International Paper Co.

Koppers operates the most facilities, 20, and controls about 20 percent of the industry capacity. Over fifty percent of the industry capacity is held by the ten largest firms (USDC 1985).

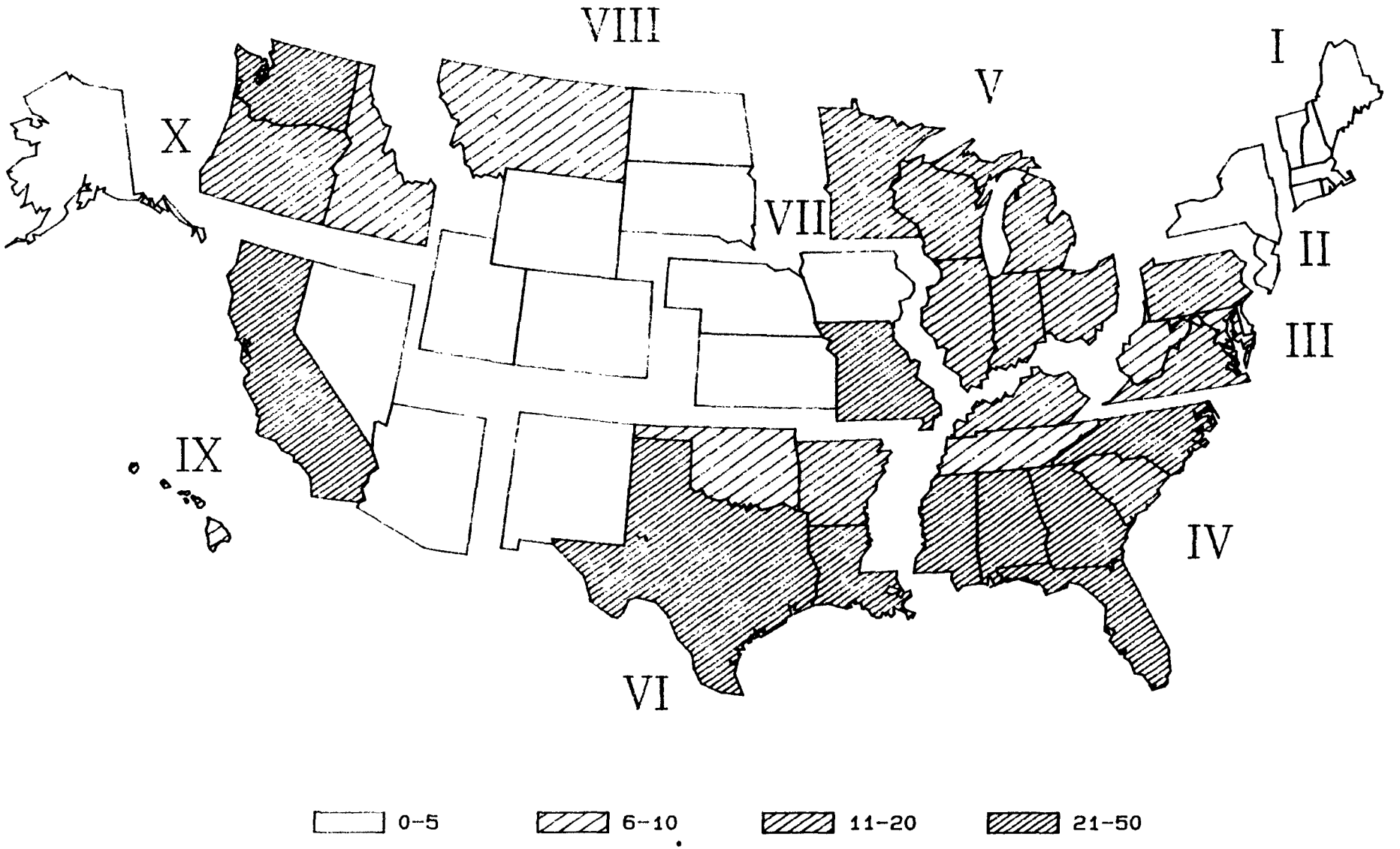
3.3 Geographical Distribution

Due to the expense of transportation, wood preservers tend to be located close to timber cutting operations. Over seventy-five percent of all facilities are located in two regions: a) from east Texas to Maryland, and b) the northern Pacific Coast (USEPA 1980). Approximately 33 percent of all wood preserving sites are located in five states (Georgia, Alabama, Louisiana, Mississippi, and Florida), with 57 percent being located in ten states. Distributions by EPA region are shown in Figure 3-1 and Table 3-2 below.

Table 3-2 Location of Facilities by EPA Region

EPA Region	No. of employees per facility		
	Total	1-19	20+
I	5	5	0
II	10	10	0
III	51	26	25
IV	170	102	68
V	71	49	22
VI	83	50	33
VII	26	19	7
VIII	21	21	1
IX	43	37	6
X	44	21	23
National	524	339	185

Source: American Wood Preservers Association Statistics for 1981 (AWPA 1982) adjusted to reflect data in the 1982 Census of Manufacturers (USDC 1985) and industry comments.



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Roman numerals show EPA regions

Figure 3-1 Wood Preserving Plants in the U.S.

4. PRODUCTS AND THEIR USES

Historically, railroad ties, utility poles, and pilings treated with creosote or pentachlorophenol (PCP) have been the major products of the industry. In recent years, lumber and plywood treated with chromated copper arsenate (CCA) has experienced rapid growth. Table 4-1 lists the major products and use distribution of the wood preserving industry in 1981.

Table 4-1 1981 Preserved Wood Products and Use Distribution

Item	Preservative, Percent			Treated Volume
	Creosote	PCP	CCA	million cu. ft.
Crossties	97.3	2.7	-	103.9
Switchties	95.2	4.8	-	6.6
Pilings	65.0	11.7	23.3	13.1
Marine				33%
Foundation				48%
Not Specified				19%
Poles	30.0	48.7	21.3	63.7
Utility				78%
Construction				10%
Not Specified				12%
Crossarms	4.4	93.3	2.3	2.2
Lumber and Timber	5.4	6.4	88.2	129.0
Fence Posts	22.3	31.7	46.0	16.5
Other	-	-	-	14.8

Source: American Wood Preservers Association Statistics for 1981 (AWPA 1982).

5. RAW MATERIALS

In the U.S., the major raw materials used to preserve wood are creosote, creosote/coal tar, or pentachlorophenol (PCP) dissolved in a petroleum based solvent, or inorganic arsenicals such as chromated copper arsenate (CCA) dissolved in water. During the last 15 years, use of CCA treated wood for construction has increased by about 800 percent (AWPA 1982). However, the use of creosote and PCP has only lessened by

about 10 percent during this period. Annual nationwide consumption rates of raw materials used to preserve wood are shown in Table 5-1 below.

Table 5-1 Raw Materials Used by the Wood Preserving Industry in 1981

Materials	Usage
Creosote	
Straight	45.9 million gallons
with Coal Tar	65.2 million gallons
with Petroleum	38.5 million gallons
Pentachlorophenol	
PCP	33.2 million pounds
Petroleum	52.2 million gallons
Waterborne Preservatives	
Ammoniacal Copper Arsenate	1.2 million pounds
Chromium Copper Arsenate	46.4 million pounds
Flame-Retardants	22.3 millions pounds

Source: American Wood Preservers Association Statistics for 1981 (AWPA 1982).

Also of importance are the types or species of wood used to produce a given product. Items made from Douglas fir or southern pine (pilings, poles, lumber and timber, crossarms, and fence posts) can be treated with any one of three preservatives. Items made of oak or mixed hardwood (crossties and switchties) are commonly treated with creosote or PCP only. Use of CCA tends to make wood surface harder or more brittle, so that its use may be inappropriate for some applications. Table 5-2 lists the breakdown of products by wood type and preservative used.

Table 5-2 Percentage Market Shares of Wood Products and Wood Treatments by Type of Wood

Product	Wood Type						Total[a]
	Douglas Fir	Southern Pine	Other Pine	Oak	Mixed Hardwood	Other	
Crossties	0.6	1.2	0.3	16.8	10.5	1.6	31.0
Switchties	-	0.1	-	1.0	0.7	0.2	2.0
Pilings	0.7	3.2	-	-	-	-	3.9
Poles	1.9	15.4	1.1	-	-	0.6	19.0
Crossarms	0.5	0.2	-	-	-	-	0.7
Lumber and Timber	3.5	31.9	0.4	0.4	-	2.3	38.5
Fence Posts	0.1	4.4	0.3	-	-	0.1	4.9
TOTAL	7.3	56.4	2.1	18.2	11.2	4.8	100.0

Treatment Type	Wood Type						Total[a]
	Douglas Fir	Southern Pine	Other Pine	Oak	Mixed Hardwood	Other	
Creosote	30.3	17.4	14.3	94.0	99.1	38.9	42.4
PCP	20.1	18.3	32.2	5.2	0.9	20.6	14.5
CCA	49.6	64.3	53.5	0.8	-	40.5	43.1

Source: American Wood Preservers Statistics for 1981 (AWPA 1982).

(a) Market share based on Table 4-1; excludes "Other" products.

6. PROCESS DESCRIPTION

Descriptions of the wood preserving processes can be found in the open literature (Wilkinson 1979, USEPA 1973, Thompson 1973a, Hunt and Garratt 1953). However, it should be mentioned that none of these descriptions were viewed as being complete. Wood preserving is a complex process and the nature of the wood treated, preservative used, and product produced can have a large influence on the ways in which the wood is treated. Very few descriptions accounted for these factors. In addition, process changes that have been made by the industry in the last few years to comply with air and water discharge regulations have had a large impact on the ways a facility handles its waste. The following description relies on the available information, engineering judgement, and inputs from industry. The description is generic and it does not necessarily represent the operations at any one given facility. Figures 6-1 and 6-2 present block flow diagrams of pressure treatment facilities using oil-based and water-based preservatives.

Before wood can be preserved, it must be preconditioned. Preconditioning of wood reduces the wood's inherent moisture content and improves treatability. The methods used to pretreat or condition wood usually depend on the type of wood being treated. These conditioning methods are:

- Ambient drying of the wood in an open yard (oak and mixed hardwoods).
- Kiln drying (Douglas fir and southern pine).
- Steaming the wood at elevated pressure in a retort (pressure vessel) followed by vacuum (southern pine).
- Heating the wood in a preservative bath under reduced pressure.
- Heating the wood by means of a solvent vapor.

In the U.S., most wood is preconditioned by ambient drying in open yards, kiln drying, or by steaming. Steaming helps to dry out the wood and makes it more permeable to oil-based preservatives. For southern pine, steaming is usually performed if the wood is to be treated with creosote or PCP. Douglas fir, oak, and mixed hardwoods or woods treated with water-borne preservatives are seldom steamed.

Steaming is usually performed in the same retort that is used for treating the wood with preservative. Wood is placed or stacked onto a tram and the tram carries the wood into the retort. Three different methods are used to steam wood. They are:

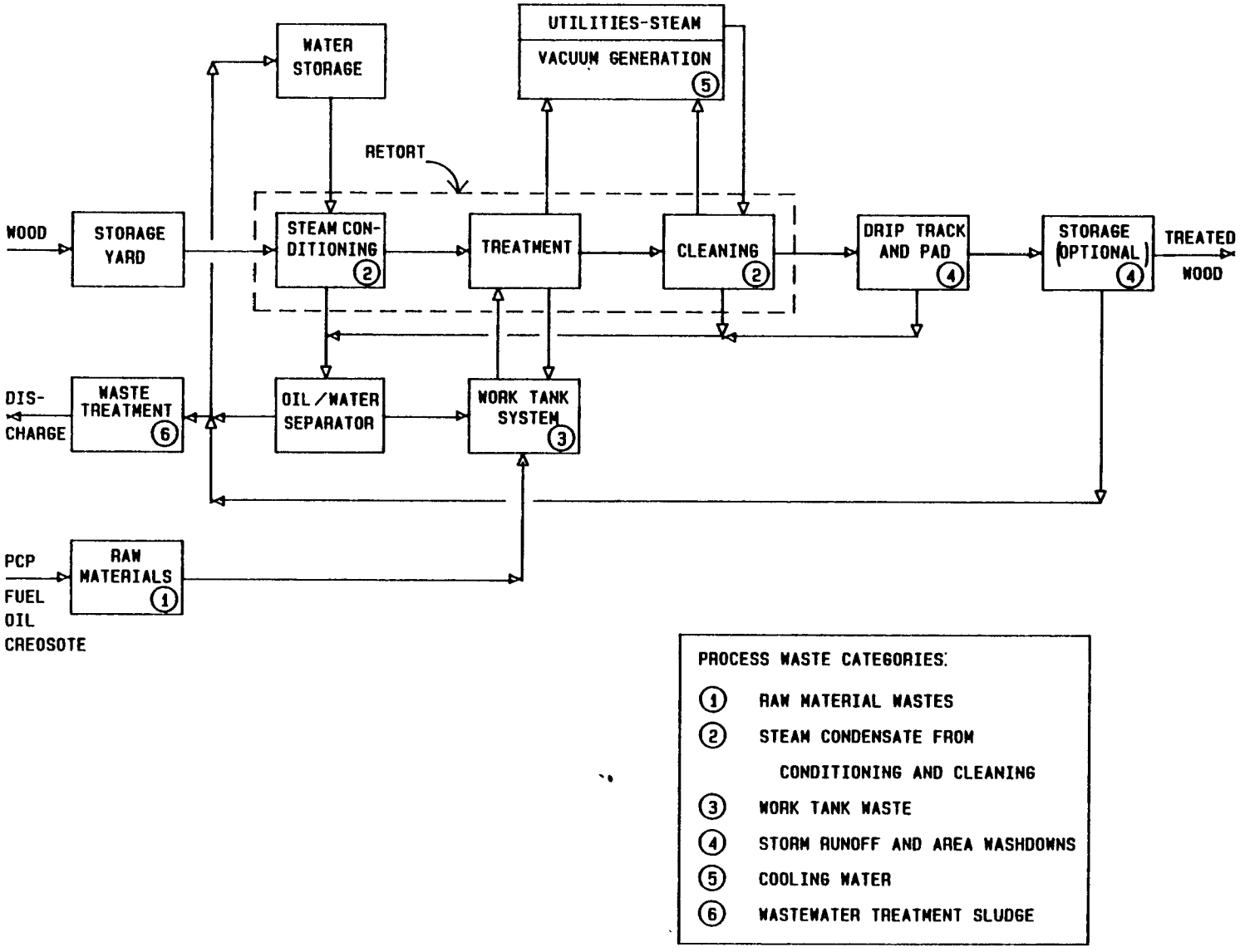

Figure 6-1 Block Flow Diagram for Oil-Based Pressure Treatment System with Closed Steaming

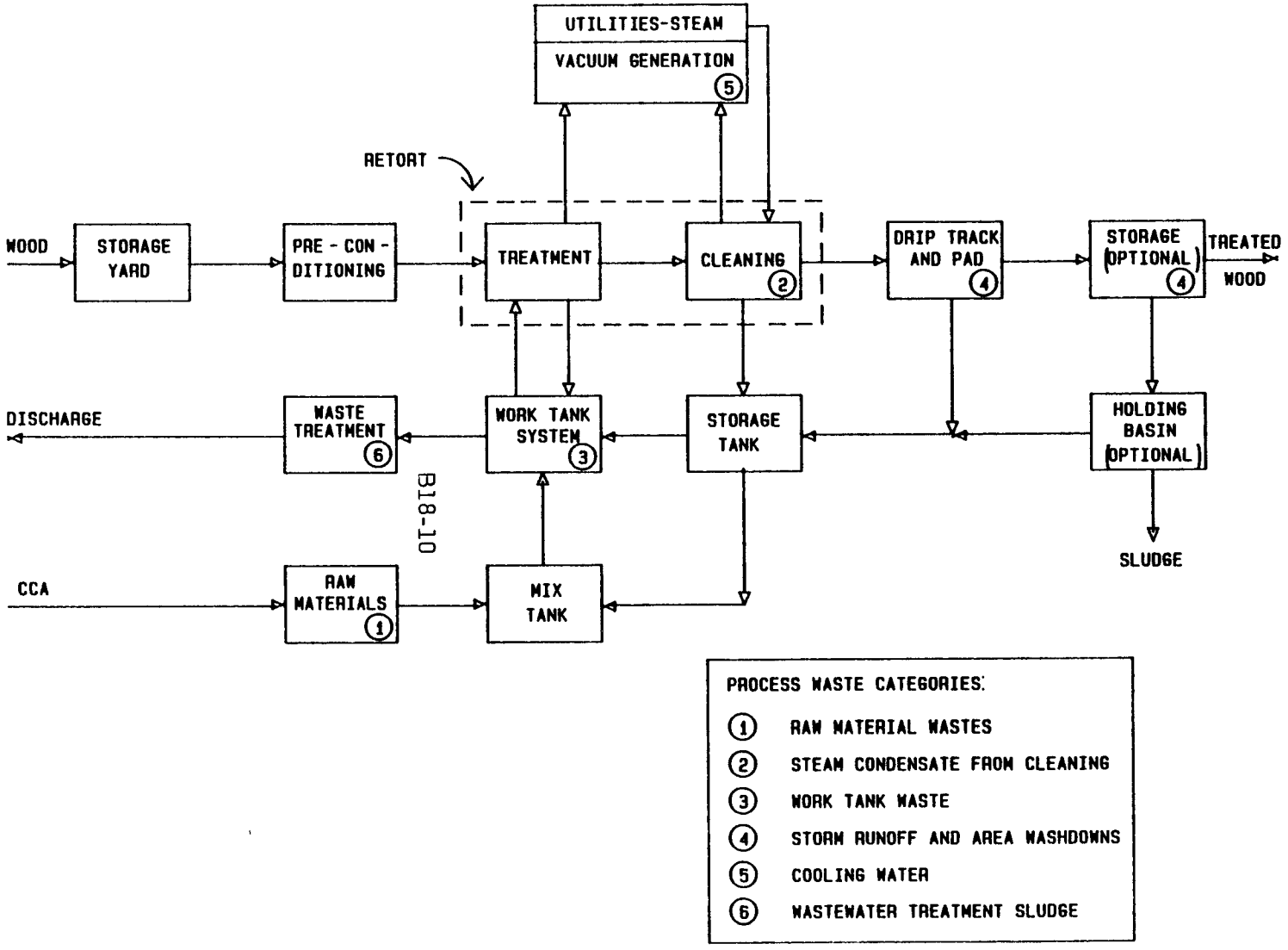

Figure 6-2 Block Flow Diagram for Water-Based Pressure Treatment System

- Open Steaming - The wood is placed in a retort and steam is applied for up to fifteen hours, during which time the condensate is collected and discharged from the retort to an oil/water separator. The separator recovers the preservative washed from the retort and sends the water on to wastewater treatment.

- Closed Steaming - The wood is placed in a retort with internal heating coils and the retort is filled with water until the heating coils are covered. Steam inside the coils causes the water outside the coils to boil, thereby generating the steam used to condition the wood. Upon completion, all of the water is drained from the retort to an oil/water separator and then back to a storage tank for reuse. Since the levels of wood sugar and acids in the water build up over time, some water is periodically removed from the tank and treated as wastewater.

- Modified Steaming - The wood is placed in a retort and steam is applied until the condensate covers the heating coils. When the coils are covered, the flow of steam into the retort is diverted to the heating coils. Upon completion, all condensate is drained from the retort and sent to the oil/water separator. Preservative is recycled to the process and the water is sent to wastewater treatment.

Following the preconditioning operation, the wood is treated using either pressure or non-pressure methods. Non-pressure methods are usually applied to wood that has been air or kiln dried only and are intended for use where deep penetration of the preservative into the wood is not required. The non-pressure methods used for applying preservatives include:

- Brushing or spraying
- Dipping
- Soaking
- Steeping

Pressure methods are used when a deeper penetration of preservative is required. In the past, many facilities operated production lines that utilized creosote PCP, and CCA in all possible permutations. While the production line utilizing water-based

preservative was segregated from the oil-based production line, some waste handling problems did occur. Today, most facilities employ only one type of preservative. Depending on the degree of penetration required and the preservatives used, two different pressure treatment processes are practiced.

The full-cell, or Bethall process, maximizes impregnation of the wood with oil-based preservative and therefore is used on wood exposed to extreme environmental conditions (e.g., marine pilings). The wood is first subjected to a high initial vacuum, causing air trapped within the cell walls of the wood to expand and diffuse out of the wood. Next, without allowing air to enter the retort, the retort is filled with preservative solution until the pressure reaches 125 to 200 psig. Because of the initial vacuum, the wood cells fill with preservative as the pressure is increased. If needed, steam may be applied to the heating coils and the temperature maintained at 180°F to 200°F for several hours. Following this heating operation, the retort pressure is released and the preservative is drained back to the storage tank. A final steaming and vacuum cycle may be applied to maximize the recovery of unabsorbed preservative and to produce a "clean" wood product. This steaming and vacuum operation helps remove preservative ("kick-back") that may drip from the wood during its removal from the retort. As an added precaution, wood removed from the retort is allowed to remain on the drip pad for several hours following treatment. The drip pad provides a means of recovering preservative or "kick-back" that would otherwise be lost in the yard. Following this operation, the wood is either held for storage in the treated wood storage yard or shipped immediately to the customer.

For wood preserved with CCA, the full-cell process is normally employed. Wood is placed inside the retort and the retort is filled with preservative. Steam is applied to the heating coils and the temperature and pressure are maintained for several hours. During this time, preservative solution diffuses into the wood and reacts with the acids formed from wood sugars that have broken down (the CCA is said to be "fixed" in the wood). After a given period of time, the solution is drained back to a storage tank (for reuse) and a short steaming and vacuum cycle may be applied. The wood is then removed from the retort and allowed to remain on the drip-pad for several hours or more while the process of fixation continues. From the pad, the wood is either stored in the treated wood storage yard or shipped directly to the customer.

For wood subjected to less extreme environmental conditions or requiring less penetration of oil-based preservative, the empty cell, or Rueping process is used. After conditioning the wood, the retort is pressurized with air. This causes contraction of the air trapped within the cell walls of the wood. Preservative is added to the retort and the pressure is increased to about 150 psig for two to eight hours. Following this operation, the pressure is released and the preservative is drained from the retort back to a storage tank. Because of the initial pressurization with air, releasing the pressure causes the air within the cell walls to expand and hence leave the cell "empty" of preservative. While wood treated with the empty cell process has a lower tendency to produce "kick-back", a final steaming and vacuum may still be applied to the retort. Following this operation, the wood is handled in the same manner as before.

7. WASTE DESCRIPTION

The primary wastes associated with wood preservation are listed in Table 7-1, along with their process sources. Most of the streams generated are high volume water streams with various levels of preservative concentration. While many of the specific process streams only contain water, wood products (primarily acids and sugars), and the preservative in use, streams such as storm runoff may contain both oil-based and water-based preservatives. The source of this cross contamination is due to rainwater flowing over areas where leaks, spills, and kick-back of different preservatives from freshly treated wood has occurred. The widespread installation of drip tracks and pads during the last ten years and the current trend of using only one type of preservative in a plant are viewed as important steps towards reducing and eliminating the occurrence of cross-contamination.

Many wood treating facilities receive their raw materials in bulk. CCA is normally sold as a 50 percent concentrate shipped by tank car, with a minor portion sold in 55 gallon drums. This concentrate is usually mixed with recycled process water and pumped to the work tank as needed. Creosote is purchased in bulk and may either be mixed with coal tar and petroleum at the facility or by the supplier. PCP may also be purchased in bulk liquid form (must be heated during transport) but is more commonly supplied in 1000 to 2000 pound blocks or in solid prill or flake form. Solid PCP is dissolved in heated fuel oil, and sent to the work tank as needed.

Table 7-1 Wood Preserving Process Wastes

No.	Waste Description	Process Origin	Composition	RCRA Code
1.	leftover raw materials in original containers	unloading of materials into mixing tanks	containers with a few ounces of CCA or PCP remaining inside	--
2.	process steam condensate	preconditioning	water with creosote, PCP, wood fiber, silt, sugars, acids, and oil	--
		cleaning	water with preservative, wood fiber, silt, sugars, acids and oil	--
3.	sludge from work tank system	filtering of preservative	preservative with wood fiber, silt, and dirt	--
4.	storm runoff and area washdowns	spills from around retort cylinder door, drippings from treated wood, equipment leaks	water with preservative	--
5.	cooling water	vacuum generation	water with preservative due to direct contact or leaks	--
6.	wastewater treatment sludge	primary treatment	lime or polymer with emulsified oils, wood fiber, silt, and preservative	K001
		secondary treatment	activated carbon, biological sludge, etc.	--

For facilities that use small amounts of preservative, CCA and PCP can be supplied in bags or drums. Once emptied, these containers would still contain traces of preservative. From the industry comments obtained, it appears that current use of bags or drums is extremely small (though use was more common in the past). However, since a recent settlement agreement between the AWPI and the USEPA (USEPA 1985) spelled out the ways in which CCA and PCP supplied in bags must be handled, it is viewed that the use of bags (and/or drums) has not been entirely eliminated.

Steam condensate from conditioning operations would contain high levels of oil-based preservative, wood fiber, silt, wood sugars, acids, and oil. The preservative washed from the retort is present because the same retort is used to condition and treat the wood. Depending on the method used (open, closed, or modified), the total stream volume can vary widely. Closed steaming, now the most widely used method, takes advantage of recycling the water used for conditioning. Since the level of wood sugars in the condensate builds up over time, some water is periodically purged or bled to wastewater treatment. The total volume of this purge stream, however, is considerably less than the volume of water sent to treatment by open steaming. Regardless of the steaming method employed, all condensate passes through an oil/water separator to provide for recovery of preservative.

For a facility using an oil-based preservative, steam condensate from the cleaning operation would be very similar to the condensate produced during conditioning. The major difference would be the lower level of acid and wood sugar present since the cleaning operation is not as severe as conditioning. This stream is handled in the same ways as before. Steam cleaning condensate from CCA or water-based facilities would contain preservative, wood sugar, and acid. This stream is usually sent to a recycle water storage tank and used for solution make-up.

Work tank waste is the result of dehydration (for oil-based preservative) and filtration operations. Oil-based preservatives recovered from the oil/water separator are heated to drive off water. The preservative, free of water, is then filtered to remove dirt, silt, and wood fiber and is stored in a heated work tank. Water-based preservative is also filtered to remove dirt, silt and wood fiber. While the amount and disposal method used for this waste stream is unknown, it is expected that the volume of this

stream would be comparatively small and that it would be either treated and/or disposed of along with the wastewater treatment sludge.

Storm runoff and area washdowns was considered by industry personnel to be the largest wastestream generated at any facility. Rainfall flowing across the drip track and pad picks up preservative that was "kicked-back" from the wood. For facilities using oil-based preservatives, this stream is sent to oil/water separation (for recovery of preservative) and then on to wastewater treatment. Runoff at facilities using water-based preservatives direct the flow into the recycle water storage tank for subsequent use.

Depending on local rules and regulations, runoff from the treated yard storage area must also be collected and treated or recycled. While the amount of preservative that may leach from the wood is very low, all of the preservatives exhibit a certain degree of solubility in water. In addition, the ever present potential for "kick-back" occurring in the yard and the past practice of not providing drip tracks and pads means that some areas of the treated wood storage may be contaminated with preservative.

Cooling water blowdown from open circulating systems should always be treated whenever the potential for contact with preservative exists or whenever chromate corrosion inhibitor is used. In the past, steam jets with single-pass barometric condensers were used for vacuum generation. Single pass barometric condensers used large volumes of cooling water and permitted direct contact between cooling water and process vapors. Today, most facilities employ recycling of barometric cooling water (only a small amount of blowdown would be necessary to purge the system) or have replaced barometric condensers with surface condensers (where mixing of cooling water with process vapors is avoided). While cooling water waste is normally sent to the process water recycle tank for reuse in a facility using water-based preservatives, cooling water contaminated with oil-based preservatives is sent to wastewater treatment.

Wastewater treatment generally can consist of primary, secondary, and tertiary treatment systems. For oil-based preservatives, primary treatment consists of flocculation with lime (used very little now) or with polyelectrolytes. The sludge produced from this operation is RCRA waste "K001" and is disposed of in a secure landfill. Wastewater from a water-based preservative operation contains copper,

chromium, arsenic, and other heavy metals. Treatment can be performed by adding sulfuric acid to the water and lowering the pH to 4.0 or less. Sulfur dioxide is then used to further lower the pH of the water and to reduce the hexavalent chromium to its trivalent form. Next, the pH is raised to 7.0 or 8.0 using caustic or lime to precipitate chromium and copper. Arsenic will also precipitate if lime is used. The remaining chromium, copper, and arsenic are precipitated using hydrogen sulfide or sodium sulfide. The produced sludge is disposed of in a RCRA permitted landfill.

The objective of secondary treatment is removal of any dissolved organic matter remaining in the water. Common methods are bio-oxidation (activated sludge), chemical oxidation, and activated-carbon adsorption. Other methods include use of sand bed filters, spray fields, and evaporation in cooling towers. Methods used in the past have included lagoons and evaporation ponds but these methods (including many being currently used) have come under close scrutiny and regulation. Water from these operations normally undergoes tertiary treatment or discharge to a POTW (Publicly Owned Treatment Works).

8. WASTE GENERATION RATES

The wood preserving industry generates 5.5 million gallons of wastewater per day (Thompson 1973a). Depending on which preservative a facility uses, the wastewater generated can contain high levels of creosote, PCP, oil, CCA, wood sugars, and acids (from the wood). Since the quantity of wastewater generated is a function of conditioning method, moisture content of the wood, rainwater drainage, and other various waste streams (cooling water, boiler blowdown, etc.), the quantity of wastewater generated by different facilities can vary drastically. Typically, the amount of wastewater generated by a facility using CCA is much less than a facility using creosote or PCP. This is because much of the wastewater generated can be used in subsequent formulations of CCA solution.

Based on a review of the available literature, no overall generation rates for each waste stream were in evidence at the time of final report preparation. Fractional waste generation rates were estimated by project staff based on review of the data, engineering judgement, and inputs from industry and are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

Waste reduction has been conceptually addressed using three approaches: (a) how to reduce the amount of toxic material entering a waste stream, (b) how to maximize the separation and subsequent recycle of toxic material back to the process, and (c) how to avoid excessive water use. This last point requires some clarification. Reducing the amount of water contacting the preservative will reduce the amount of sludge precursors that dissolve in it and may also lower their entrainment. As a result, the total organic or inorganic carry-over into the treatment system is reduced and sludge volume is minimized.

The following sections discuss waste reduction methods both identified and suggested for the main wood preserving process waste streams. These streams include raw material wastes, wood conditioning condensate, storm runoff and area washdown, and cooling water blowdown. Sludge due to wastewater treatment has not been included since its generation is directly to these other wastes. By reducing the amounts of aqueous waste produced, and hence treated, the amount of wastewater treatment sludge will decrease accordingly.

9.1 Description of Techniques

The list of individual primary waste streams and their sources, along with a list of source reduction methods, is presented in Table 9-1. The following sections discuss noted waste reduction methods and procedures. The basis for identification came from published accounts in the open literature and communications with the industry.

In addition to the waste reduction measures classified as process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" have also been included. Good operating practices are defined as procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practices:

- o Waste stream segregation
- o Personnel practices
  - Management initiatives
  - Employee training

- o Procedural measures
  - Documentation
  - Material handling and storage
  - Material tracking and inventory control
  - Scheduling
- o Loss prevention practices
  - Spill prevention
  - Preventive maintenance
  - Emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Raw Material Wastes

In the U.S., most creosote, PCP, and CCA is sold, transported, and stored in bulk. However, some small scale wood preservers purchase PCP and CCA in 50 pound bags and drums. Since an ounce or two of preservative remains inside the bag after being emptied, the entire bag may be classified as being hazardous. If these bags come in contact with non-hazardous material, then all of the material might be considered hazardous. In addition, spills of preservative in the mix tank area can lead to area contamination, increased wastewater generation (due to rainwater and area clean-up), and undue worker exposure. While most liquid formulations are handled in automated, closed systems, many powder handling operations are still manual. This includes facilities receiving powder or dry preservatives in bags, drums, and in bulk. The following source reduction methods for facilities purchasing powder or dry preservatives (prilled or flaked PCP and inorganic arsenicals) have been noted:

- o Purchase of materials in bulk.
  This is by far the most commonly used method in the industry. By receiving raw materials in bulk, no container waste is generated and the degree of manual handling (and hence the degree of spillage) is reduced.

- o Use of closed systems for powders.
  After September 1, 1987 the use of closed systems for unloading and mixing prilled or flaked PCP must be installed at all facilities using

powdered PCP (USEPA 1984). The system would consist of pneumatic equipment design to convey the PCP directly from a hopper truck or railroad car to a closed (dissolving) mixing tank. The cost for this system was estimated to be $10,000. Closed systems are also required for handling dry inorganic arsenicals but since their use is considered to be widespread, no deadline was set.

For facilities purchasing preservative in bags or drums, closed systems are also available. For CCA, use of in-drum mixers to prepare solutions has been documented in the open literature (Wilkinson 1979). The unit consists of a small pump and a concentric pipe that is screwed into the drum's bung hole. Water is pumped into the drum and then into the treatment cylinder or retort. Final rinse water is also pumped into the drum and used as make-up solution. A pneumatic system was also described for use with powder formulations supplied in bags.

- Use of rinseable/recyclable drums with plastic liners instead of paper bags

- Better operating practices.
  Through industry contacts in the paint manufacturing industry (an industry characterized by a high degree of powder handling from paper bags), it was established that the most effective way of reducing hazardous waste associated with bags and packages was to segregate the hazardous materials from the non-hazardous materials. As an example, empty packages that contained hazardous materials should be placed into plastic bags (so as to reduce or eliminate dusting that leads to contamination of non-hazardous materials) and should be stored in a special container to await collection.

9.1.2 Wood Conditioning Condensate

Since the same retort is used for steam conditioning and treatment, preservative remaining in the retort from the last treating operation is washed out with the steam condensate. While much of the preservative is recovered by sending the wastewater to an oil/water separator, some of the preservative is lost because of oil/water emulsions that are difficult to separate. For facilities using CCA, steam condensate is not

produced since the wood is seldom steam conditioned. The source reduction methods considered for facilities using creosote or PCP are listed below:

- Reduction of steaming by use of air or kiln drying.
  By increasing the use of air or kiln drying and thereby reducing the need for steaming, generation of a major wastewater stream can be avoided. Because the effectiveness of air drying is limited to only a few geographic locations, many facilities have installed drying kilns instead (Thompson 1973a). While kiln drying has several advantages over air drying (increased production rate and reduced yard inventory), its use is limited to mainly items made of Southern pine such as pilings, poles, and timber. Products such as crossties and switchties do not readily lend themselves to kiln drying, since the hardwoods used to produce these items will crack and warp when kiln dried.

- Use of separate retorts for steam conditioning and treating.
  Another way of reducing the waste associated with steam conditioning is by physically separating the conditioning operation from the treatment process (Van Frank and Eck 1969). By preventing the preservative from mixing with the steam condensate, this waste stream would no longer contain preservative. Apart from added capital cost, the major disadvantage of this method is the increase in time it takes to transfer the wood from one retort to another. During this time, the wood will cool and therefore some steaming of the wood will be required during treatment (southern pine must be treated while hot to prevent formation of sludge). In addition, many facilities have only two or three retorts and thus would have to buy additional equipment.

- Conversion from open steaming to closed steaming.
  By far the most popular method of reducing waste associated with conditioning has been the conversion from open to closed (or modified) steaming (Thompson 1973b). Converting from open to closed steaming requires only the installation of a storage tank for the recycled condensate. Conversion to modified steaming, while not as effective, requires only some piping modifications. In addition to the reduction in wastewater generated, (it is estimated that facilities using open steaming generate

2.43 gallons of wastewater per cubic foot of wood treated, closed steaming facilities generate 0.45 gal/ft^3, and modified steaming facilities generate about 1.0 gal/ft^3 (USDC 1983)), it is also possible that the resulting wastewater is easier to treat. Studies have shown that emulsification of oil in water apparently results from violent agitation of the oil and water when passing through a steam trap (Thompson 1973a). When closed or modified steaming is employed, the water in the retort can be drained through a discharge pipe as opposed to a steam trap orifice. By proper piping design and using a full port ball valve for on-off level control so as to minimize agitation, the amount of oil in water emulsion formed can be reduced.

- Use of air-flotation on the oil/water separator effluent.
  By installing an air-flotation (dissolved-air or induced-air type) unit on the effluent from the oil/water separator, an increase in recovery of the preservative can be achieved. The float material produced (preservative, water, and air) would be mixed with the preservative recovered from the separator and sent to the work tank system for dehydration, filtering, and reuse. API separators, followed by air-flotation units, are quite common at many oil refineries.

- Use purer preservatives.
  By using purer preservatives, the total amount of toxics entering a wood preserving facilities wastewater could be lowered. As recently reported, the USEPA wants suppliers of pentachlorophenol to lower the level of hexachlorobenzo-p-dioxin (H_xCDD) present in the preservative from 15 ppm down to 1 ppm (USEPA 1984). The authors of this report believe that further investigation of preservative purification by the suppliers is warranted. While increasing the degree of purification required may lead to increased waste production at the supplier facilities, it is believed that they are in a much better position to properly handle the resulting waste.

9.1.3. Sludge from Work Tank System

Before preservative can be reused, it usually undergoes some form of treatment. For oil-based preservatives, treatment usually includes dehydration and filtering. For

water-based preservatives, treatment can consist of pH adjustment followed by filtration. The ways in which sludge from the work tank system can be reduced are:

- o Clean the wood prior to insertion into retort.
  By ensuring that the least amount of dirt, silt, and loose wood fiber enters the retort before treatment, the least amount of sludge will be produced. Treatment of dirty wood should never be allowed (Wilkinson 1979).

- o Better operating practices.
  Also to be avoided is treatment of unseasoned wood, long soaking, contamination of treating solution, and incomplete mixing of preservative. Since treatment and disposal of sludge represents a loss of valuable raw material (preservative), efforts are made to minimize its production. Dust entrainment into solution can be avoided by constructing windwalls around the drip-pad area. Frequent cleaning of drip-pads and use of covers will help to prevent dirt from getting into solution.

9.1.4 Storm Runoff and Area Washdowns

Water that contacts freshly treated wood or flows across plant areas contaminated with preservative constitutes part of the wastewater generated by a facility. For most plants, the major source of area contamination is due to preservative dripping from treated wood. In the past, this preservative would drip in the treated wood storage yard and contaminate the area. Today, most facilities have installed drip tracks and pads so that the drippings can be collected and reused. For facilities using CCA, area contamination used to occur when the retort door was opened and some of the solution spilled out. Nowadays, spill basins have been installed so that spilled solution can be recovered and reused. Other sources of area contamination are due to equipment leaks and spills. The following source reduction measures were noted for reducing wastes associated with storm runoff and area washdowns:

- o Install drip tracks, pads, and spill basins.
  This method is widely used by the industry and was among one of the first waste minimization measures undertaken (Van Frank and Eck 1969; Morgan and Burdell 1978).

- Covering the pad and treated wood storage area.
  By covering the pad and treated wood storage area, less contaminated rain water would have to be collected and treated. In addition, the collection of dirt and silt would also be reduced so that less work tank sludge would be generated. While this method has been identified as having been used by the industry (Thompson 1973a, Wilkinson 1979), the cost of covering the yard could be prohibitive.

- Divert storm water away from contaminated areas.
  For facilities with large areas of contamination (old holding ponds and lagoons, for example), diversion of clean storm water away from the area reduces the amount of runoff that must be collected and treated (Morgan and Burdell 1978). In addition, reduction of these flows also allows for more reliable and consistant operation of the wastewater treatment system, since it is less subject to overloading.

- Better operating practices.
  According to obtained information, most wood is left on the pad for several hours following treatment. During this time, oil-based preservatives "kick-back" and drip onto the pad, while water-based preservatives become "fixed" and their leachability diminishes. Following this period, the amount of preservative that drips or leaches from the wood is extremely small. However, it was reported that water-based preservatives can leach from wood for up to one week after treatment (Wilkinson 1979). Therefore, maximizing the amount of time the wood is allowed to remain on the pad is essential for maintaining a clean treated wood storage area.

  Other related methods include proper stacking of the wood in the retort so that the preservative can drain freely, use of a higher degree of vacuum to remove unabsorbed preservative, use of dry clean-up methods for drips and spills occuring off the pad, minimizing water use for cleaning the pad, and always ensuring that the wood produced is clean. While the USEPA tried to specify approaches which assure production of clean wood, the AWPI recommended that particular methods not be specified, due to the diverse and complex nature of the process (USEPA 1984). Instead, it was recommended that facilities adhere to clean wood standards (AWPA

standard C-1, for example) which only set the degree of cleanliness required and not the ways to achieve it.

9.1.5 Cooling Water

For facilities that use single-pass systems, barometric condensers associated with vacuum generation via steam-jets can be a large source of wastewater. Barometric condensers permit direct contact between cooling water and process vapors. While the resulting level of water contamination is lower than the retort effluent, this stream still represents a major wastestream requiring treatment. The following source reduction methods for reducing wastes due to contaminated cooling water were noted:

- Replace barometric condensers with surface condensers.

- Construct cooling water reuse systems.
  In 1974, 41 percent of all plants employed surface condensers (in which there is no contact between cooling water and the process vapors), 41 percent employed barometric condensers, and 18 percent did not use condensers (Thompson 1975). Compared to a 1972 survey (Thompson 1973b), the number of plants using barometric condensers was decreasing, and 84 percent were recycling their cooling water. Therefore, it appears that industry has widely implemented the above two measures.

- Use vacuum pumps instead of steam jets.

- Use of non-chromate cooling water treatment.
  For facilities using oil-based preservatives, use of non-chromate cooling water treatment for corrosion inhibition would eliminate the need for treating cooling tower blowdown for chromium. For facilities where water-based preservatives are used, the amount of chromium in the treatment sludge would be reduced.

- Better preventive maintenance.
  Another method that deserves special attention is the effect that better preventive maintenance can have on the contamination of cooling water. Wilkinson (1979) and Thompson (1973a) stress the importance of detecting

leaks in process equipment so that preservative loss can be minimized. By reducing the amount of preservative that leaks into the cooling water, the overall requirements for treatment can be reduced.

9.2 Implementation Profile

The wood preserving industry has implemented many measures to reduce the amounts of waste produced. Some of the most effective measures include: purchasing of raw materials in bulk; converting from open to closed steaming; installation of drip tracks, pads, and spill basins; and replacement of barometric condensers with surface condensers. Additional measures that could result in future reductions include the use of closed systems for powder handling, use of air flotation on oil/water effluent, covering of the pad and treated wood storage area, and use of non-chromate water treatment chemicals. While the costs for some of these methods could be quite low (the USEPA estimated that the cost for a closed powder handling system would be 10,000 dollars), others could be very expensive (covering of the treated wood storage yard). The cost of each method would have to be weighed against the cost savings in waste treatment and disposal. Since operating facilities have already installed waste treatment systems to achieve regulatory compliance, some of the proposed methods might be hard to justify economically. For facilities under design, incorporation of the proposed methods could be more cost-effective.

9.3 Summary

Table 9-1 presents summary data on wood preserving waste sources and control methods. The ratings of each listed method shown in the table were based on review of the available literature and consultation with industry personnel. Each method was rated on a scale of zero to four for its effectiveness, extent of current use, and future application potential. The current and future extents of waste reduction were then derived using the methodology presented in the introduction to this appendix.

A current reduction index of 3.0 (75 percent) is indicative of the very high level to which the waste has already been minimized (CRI is a measure of the reduction of waste that would have been generated if none of the methods were practiced at their current level of application). By implementing additional waste reduction measures or increasing the use of existing measures, the amount of waste currently being

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR THE WOOD PRESERVING INDUSTRY

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Raw Material Wastes	1. Purchase raw materials in bulk	1	1	4	3	1		3.0	0 3	
	2 Use of closed systems for powder	3	2	3	2	4		1.5	1.5	1 5
	3 Use of rinseable/recyclable drums	0	0	2	0	1		0 0	0 5	
	4 Better operating practices	1	1	3	3	1		2 3	0.2	
	Overall	1 25	1.00	3 00	2 00	1.75	0 01	3.0	0 6	1 5
Wood Conditioning Condensate	1 Increase use of air/kiln drying	3	2	4	2	1		2.0	0 5	
	2. Use separate retort for conditioning	1	1	2	1	1		0 5	0 4	
	3. Convert from open to closed steaming	3	3	3	3	2		2 3	0 4	
	4. Use air-flotation on effluent	1	1	2	1	3		0.5	1.1	1 1
	5. Use purer preservatives	1	0	1	0	2		0.0	0 5	
	Overall	1 80	1 40	2 40	1 40	1 80	0 10	2.3	0.6	1 1
Sludge from Work Tank System	1 Better operating practices	3	2	3	3	1		2 3	0 2	0.2
	2. Clean the wood prior to treatment	1	1	3	3	1		2.3	0 2	0.2
	Overall	2 00	1 50	3.00	3.00	1.00	0 01	2 3	0 2	0 2
Storm Runoff and Area Washdowns	1 Install drip track, pad, spill basin	3	3	3	4	1		3.0	0 0	
	2 Cover pad & treated wood storage area	3	2	3	1	3		0.8	1 7	1 7
	3 Divert storm water runoff	3	2	3	3	1		2 3	0.2	
	4. Better operating practices	2	2	3	3	1		2.3	0 2	
	Overall	2 75	2 25	3 00	2 75	1 50	0 75	3.0	0 5	1 7
Cooling Water	1 Replace barometric condensers	3	3	4	3	1		3 0	0 3	
	2. Construct cooling water reuse system	3	3	3	3	1		2.3	0.2	
	3. Use vacuum pump instead of steam jet	3	3	3	2	2		1.5	0 8	
	4 Use non-chromate water treatment	2	2	2	0	3		0 0	1.5	1.5
	5 Better preventive maintenence	3	3	3	3	1		2.3	0.2	
	Overall	2 80	2 80	3 00	2 20	1.60	0 13	3.0	0 6	1 5
All Sources	All Methods							1.00	3.0	0 5	1 6

(*) These streams include listed "F" and/or "K" RCRA wastes

generated can be reduced by a moderate amount, as measured by a future reduction index of 0.5 to 1.6 (13 to 40 percent). The most effective measures for achieving this reduction would be to cover the pad and treated wood storage area, use non-chromate cooling water treatment chemicals, install air-flotation units on oil/water separator effluent, and install closed systems for powder handling.

10. PRODUCT SUBSTITUTION ALTERNATIVES

10.1 Steel and Concrete

Very few substitutes exist for treated wood products. Substitution of metal or concrete pilings for creosote treated wood pilings has been investigated (USDC 1983). The major conclusions of this study were that:

- Although they offer considerably longer life spans, concrete and steel pilings cost three to five times as much as wood. The overall economic analysis favors treated wood.

- While producing less hazardous waste than the wood treatment process, production of steel pilings also produces waste.

- Due to increased environmental/regulatory pressure, many wood preservers have stopped producing creosote-treated wood pilings.

Subsequent inquiries with industry revealed that environmental/regulatory pressure was not a factor for stopping the use of creosote. A subsequent study (USEPA 1984) showed that a large annual cost penalty ranging from 1.3 billion to 2.1 billion dollars would have to be incurred by consumers if treated poles were unavailable and concrete or steel had to be used. For pilings, the total annualized installed cost would increase by 33 percent for concrete and 67 percent for steel. Use of concrete for railroad ties would also result in adverse cost increases. Overall, halting the use of all wood preserving chemicals would have major economic impact nationwide.

10.2 Trends in Preservative Usage

Investigation of wood preservation statistics reveals that major changes have been taking place in the industry. While the amount of wood treated with creosote and PCP has remained relatively constant over the last 15 years, production of CCA treated wood has increased about 800 percent (AWPA 1982). Over the same time period, many new CCA-using facilities have been built and many oil-based using facilities have converted or closed. As shown in Table 10-1, the percentage of plants using creosote and PCP has dropped while the percentage of plants using CCA has increased. Also of importance is the large drop in the percentage of facilities using two or more preservatives. As a result of using a single preservative in the facility, the wastewater treatment system is expected to be more efficient and reliable because no cross contamination of materials can occur. It is also expected that the facilities' overall waste generation rate should be lower due to the standardization of preservative usage.

Table 10-1 Production Trends in the Wood Preserving Industry

	Percent of Plants	
Preservative	1974	1984
PCP	53	20
Creosote	50	24
CCA	41	81
Two or more	67	19

Source: Status of Pollution Control (Thompson 1975); Wood Preservation Statistics (Micklewright 1985).

The alternatives to most widely used preservatives (PCP, creosote and arsenicals) include naphtenates of zinc and copper. Zinc naphtenate appears to be safer than PCP while exhibiting equivalent wood preservation characteristics.

An environmental issue related to the choice of preservative is the disposal of used or spent treated wood. Disposal by incineration is an option likely to be considered as an

alternative to landfilling. While wood treated with creosote can be burned with virtually complete destruction, wood treated with PCP produces hazardous hydrogen chloride fumes which should be scrubbed and removed from the flue exhaust. Wood treated with CCA also presents a problem, since the ash produced by burning will still contain heavy metals and does require special disposal. Currently, all used treated wood is disposed of in landfills and dumps. State and federal regulations on incineration of treated wood have been promulgated (USEPA 1984, 1985).

11. CONCLUSIONS

While the wood preserving industry has achieved a large reduction in the amount of waste it produces (a current reduction index of 3.0 or 75 percent), it appears that further reductions are possible. Our estimates indicate that possible waste reductions are characterized by a future reduction index of 0.5 to 1.6 (13 to 40 percent) which is indicative of a moderate potential. Several major methods appear to be quite effective, including covering the pad and treated wood storage area, use of non-chromate cooling water treatment chemicals, and use of air-flotation on the oil/water separator effluent. Waste reductions will also occur as more and more facilities implement waste reduction programs and as older equipment wears out and is replaced. Since many of the proposed waste reduction measures are cost-effective, implementation can best be achieved through an increase in awareness.

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13. INDUSTRY CONTACTS

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GOOD OPERATING PRACTICES

1. INTRODUCTION

1.1 Purpose

This study is part of an assessment of source reduction practices in U.S. industry and is intended to complement the series of process studies in Appendix B to this volume. In the process studies, good operating practices are evaluated according to their current and potential waste reductions within the individual processes. This study seeks to generalize over these separate treatments in order to develop a more global perspective on sound waste-minimizing practices.

The purpose of this study is to identify and expand upon the elements of a set of source reduction practices which can be implemented through an organizational modification of a production operation (as opposed to technology modification or changes to input materials). In numerous case studies of successful source reduction efforts, a factor weighing heavily in the achievement of waste reduction has been a procedural or policy change within the plant or firm. In the context of waste minimization, the general objective of good operating practices or procedures is to minimize material losses and the probability of their occurence. It may have been something as simple as a change in the method of handling the hazardous materials, or something as complex as a change in management outlook. Proper procedures and policies leading to reductions in the amount of hazardous wastes generated should be considered in the overall operating plan.

This discussion of good operating practices is, by necessity, a qualitative one. Ideally, an investigation into the feasibility of making an operating change would express the end result and potential implementation quantitatively in terms of cost and other measurable quantities. This approach does not appear viable in this study for the following reasons:

- When good operating measures are implemented, it is often not possible to monitor or document the results.

- Good operating measures are often employed in conjunction with other plant changes, which makes the specific waste-reducing/cost-saving impact of the good operating measures difficult to separate from the total impact.

In sum, no solid data exist for the general role of good operating measures in source reduction. A qualitative discussion may nevertheless point out the characteristics of good operating practices. Also, the characteristics of operations which are amenable to operating improvements may be explored qualitatively.

1.2 Definitions

In the context of this study, a good operating practice is defined as a procedure or institutional policy within a service or manufacturing operation which results in a reduction in hazardous waste generation. Good operating practice relates primarily to the human aspect of production, i.e. organizational structure, initiatives, operations planning and control, as opposed to changes in technology or materials. The following is a representative list of areas which might easily lend themselves to changes in operating practices along with a brief description:

1) Material handling improvements - any change in material handling procedures which reduces the ratio of waste to material delivered.

2) Management initiatives - any revision of operational supervisory structure, schedule, or set of managerial procedures and incentives which lead to a reduction in waste per unit output.

3) Employee training - any additional training of employees or increase in employee awareness of operating practices and their impacts on waste generation which results in lower waste per unit output.

4) Scheduling improvements - tighter or more accurate operations scheduling and plant area communications which result in lower waste per unit of production.

5) Spill and leak prevention - a change in existing procedure which reduces waste resulting from spills or leaks and thereby lowers waste per unit of production.

6) Preventive maintenance - maintenance procedures designed to reduce incidences of equipment breakdown and inefficiency or of process fluid leakage, thereby lowering the amount of waste per unit output.

7) Corrective maintenance - efforts, such as resetting control valves or adjusting process temperatures, can increase productivity and prevent loss.*

8) Material/waste tracking or inventory control - any improvement in the tracking of a material's location, quality, age, use or alteration of its purchased lot sizes, which would result in lower waste per unit output.

9) Additional documentation - additional procedural guidelines or material information which results in less waste per unit output.

10) Waste stream segregation - any measure taken to isolate waste streams by 1) toxicity, 2) type of contaminant, and/or 3) physical form, which reduces the amount of waste produced per unit output.

The above elements of good operating practices are often referred to as "good housekeeping".

1.3 Format

This study is presented in three parts. The first part (Section 2) presents the types of plant operations which could minimize waste generation and describes some representative good operating practices. The division of these practices into waste stream segregation, institutional measures, procedural measures, and loss prevention programs is made according to the factor playing the largest role in their implementation: technology, personnel, procedure, or program structure. Good operating practices are in fact difficult to separate from each other because they constitute an integal part of sound overall plant operation. For example, the labels that aid in material handling serve also to track materials and control inventory. Good

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* Westinghouse Electric Corp. 1985: Personal communication.

material storage practices can be part of a spill or fire prevention program, as is preventive maintenance. Management initiatives and employee training affect all facets of plant operations and therefore all technological, procedural, and program practices.

Section 3 records some observations on good operating practices -- as they apply to different types of processes -- and draws conclusions from the foregoing exposition of individual practices in Section 2. Generic batch and continuous processes are described in terms of how the suggested good operating measures can be integrated into the production process.

Section 4 lists the references used for this study. The list reveals a reliance on material from pollution prevention programs and on specific case studies and topic treatments drawn mostly from chemical engineering publications. This material was chosen for its explanatory and illustrative value.

2. TYPES OF GOOD OPERATING PRACTICES

2.1 Waste Stream Segregation

Hazardous waste which is hauled to off-site disposal facilities is often a combination of two or more waste stream types or of one type of waste and water. Waste stream segregation as a good operating measure may involve:

- o Isolation of hazardous materials from nonhazardous materials.
- o Isolation of hazardous waste by contaminant.
- o Isolation of liquid from solid waste.

Waste stream segregation can result in smaller waste haulage volumes and easier disposal of the hazardous waste generated while producing the same amount of product. In addition, segregation can often result in simplifying waste treatment or make it easier to recover and recycle materials.

When a non-hazardous material is mixed with a hazardous material, there exists the possibility that the entire mixture must be classified as hazardous. By separating hazardous from non-hazardous materials or not allowing them to mix in the first place,

the quantity of waste requiring regulated disposal is reduced. ICI Americas, Inc., of Goldsboro, N.C., an agricultural chemical research and development firm, designates separate containers for hazardous and non-hazardous waste, thus preventing cross-contamination of the non-hazardous waste with the hazardous waste. In conjunction with a procedure for segregating chlorinated solvents from non-chlorinated solvents and a policy of returning unused chemicals to the distribution center, the overall volume of waste exiting ICI was reduced from 100 drums in 1981 to 60 drums in 1984. The product output of the firm nearly doubled in that period; observing that disposal costs doubled as well (from $120/barrel to $266/barrel), the firm saved roughly $37,000 in 1984 alone (Huisingh et al. 1985).

The isolation of hazardous waste by contaminant often allows wastes to be recycled or reused, thereby reducing the off-site disposal requirement. Rexham Corporation of Matthews, N.C., does high-tech printing and coating, including film substrate, for the photographic industry. Toluene is used to clean the ink from the press, and runoff toluene is collected as waste. Rexham has nearly eliminated its toluene waste by segregating cleanup toluene according to the color and type of ink cleaned and then reusing the collected wastes to thin future batches of the same ink (Huisingh et al. 1985). The procedure has no effect on product quality and has resulted in almost 100% reuse of the toluene solvent.

Martin Marietta Aluminum of Torrance, CA. reduced its cleaning and waste hauling costs by $50,000/year through the simple operation of filtering aluminum particles from soluble oils (Suzuki 1985). Prior to installing the filter apparatus, the company was forced to transport its oil wastes to a Class A dump site, rather than taking it to a municipal site, due to EPA regulations on effluent disposal. Disposal costs were too high. Installation of the filter cost $1,000 and was performed by Martin Marietta employees. The oil recovered from the filtering operation is reused, resulting in lower oil purchase costs and oil waste transport costs.

In paints and coatings formulation the volume of hazardous waste can sometimes be reduced by segregating empty paper bags that contained toxic pigments (such as lead chromate) from non-hazardous discards.

For segregation to be cost effective, however, the savings resulting from reuse, recycling, resale, or lower disposal costs must outweigh the costs of the additional personnel allocations and of the on-site equipment and storage facilities needed.

2.2 Personnel Practices

2.2.1 Management Initiatives

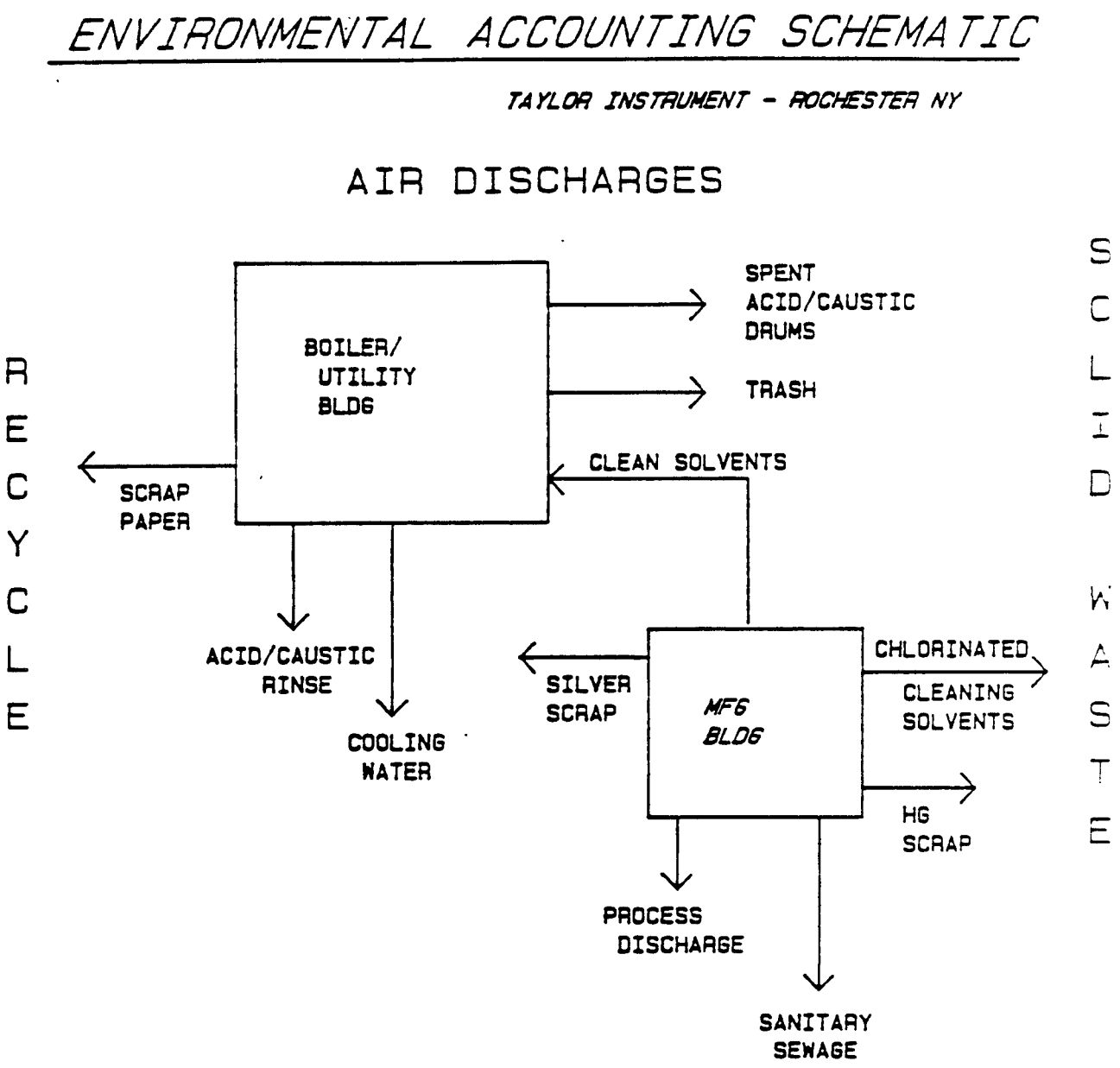
Revisions in operational supervisory structures, schedules, or sets of procedures contribute greatly to a company's efforts to reduce waste and/or come into regulatory compliance. The need to head off rising disposal costs and to confront environmental issues and responsibilities has encouraged many firms to institute self-standing environmental programs and policies. These include in-house chemical waste management programs, which can take the form of ongoing waste management/reduction programs, environmental auditing programs, or periodic environmental reviews of operations.

Waste Reduction Programs

In-house ongoing waste reduction programs can range from complex programs like 3M Corporation's Pollution Prevention Pays program, which is independently staffed and extends to 3M operations worldwide, to simple basic pollution awareness programs wherein operational managers and employees are asked to identify ways of reducing waste. Established in 1975, the 3M Corporation's 3P program has since achieved the prevention of an estimated 103,000 tons of sludge and solid waste annually. The company estimates its cumulative savings over the period at about $248 million. The savings are in the form of retained sales on reformulated products, conserved materials and energy, and the ability to delay or completely eliminate the purchase of pollution control equipment.

According to information from 3M, the initiation of a "3P" type program begins with a strong management commitment. The suggestion is to "work from the top down". The plan can be implemented beginning with an environmental audit. The wastes which emanate from the operation can be documented via an environmental accounting schematic (see Figure 2-1) and quantified, after which all costs associated with these

FIGURE 2-1 ENVIRONMENTAL ACCOUNTING SCHEMATIC



Source: 3M Corporation

discharges can be calculated. This procedure gives an overall picture of the types and amounts of waste being generated and the costs associated with generating the waste.

Once the environmental picture is established, meetings are held with laboratory, research and development, manufacturing, and process engineering personnel to identify a strategy for reducing discharges and to choose the problems and solutions on which to concentrate. At 3M, solutions generally fall into one or more of four categories: 1) product (re)formulation, 2) process modification, 3) equipment redesign, and 4) recovery/reuse. The choice of a problem and solution can be influenced by the chance of success, the potential to apply the solution to other problems, and the age of the process. At 3M, processes that have remained unchanged for 10 years are targeted.

Following the implementation of a solution, further efforts are made to recognize contributors, publicize success stories, and keep account of the quantities of waste reduced and the costs saved. In addition, the 3P program scrutinizes all new projects using 3P techniques both in the laboratory and in the initial engineering phase. In all, more than 1,500 3P projects worldwide have been approved since the program began, 323 of which were approved in 1984 and are expected to contribute $42.5 million to future cost savings in 3M's estimation. An example of a publicized 3P "success story" is given in Figure 2-2.

Other examples of in-house waste reduction programs are found at Borden Chemical Company in Fremont, CA, and at Emerson Electric Company in Murphy, North Carolina (Huisingh et al. 1985). Borden Chemical Company's management initiative consisted of process reviews by management and the educating of employees to be aware of hazardous waste reduction opportunities. As a result of this process, a 93% reduction in the organics entering the company's wastewater treatment system was realized. In Borden's case the residual phenol from the hose that conveys phenol from delivery trucks to storage tank had previously been permitted to empty into the treatment system. Currently the hose is flushed with water and the water-phenol mixture directed to a storage tank for use in the process. This change in practice came about because, 1) Borden had taught its personnel that any amount of chemical waste is important in the total amount of waste produced and 2) Borden management had "walked through" the movement of materials in the production process.

FIGURE 2-2 SAMPLE PUBLICITY FOR POLLUTION PREVENTION PROJECT

ideas

A Compendium of 3P Success Stories

Pollution Prevention Pays

Managing for a better environment

Keener Cleaner

Tank Laved, Solvent Saved, Toil Shaved

Problem

One hundred ten tons of tank cleaning solvent were being lost annually at 3M's plant in Hilden, West Germany. The plant had no solvent recovery capability so the used solution was processed by an outside contractor from whom 3M bought the recovered solvent.

Another aspect of the problem was the excessive manpower being spent to clean Hilden's two 300-gallon vessels.

Clean-up was necessary to avoid contamination of an ensuing batch when the color of a coating solution was changed. The tank was flushed with solvents and roughly cleaned by agitation of the solution-mixing propeller. Manual cleaning with brushes followed, sometimes requiring that an employee enter the tank. Cleaning a tank took three hours and the time of one employee. Annually, cleaning the plant's two tanks required 800 hours.

Solution

Hilden developed a fully-automated cleaning system in which the solvent mixture is pumped under high pressure through a rotating spray head. The old mixing tanks were replaced by new specially designed stainless steel vessels.

Solvent dispensed by rotating spray head solved Hilden's tank cleaning problems.

The spray head is portable and can be inserted in a tank by one worker in five minutes. Because the new system is closed, an operator does not have to enter the vessel to clean it and has no direct contact with solvent.

The system incorporates a sedimentation tank to recover solvent from the cleaning solution that used to be given away and bought back.

Payoff

- The new system cost $69,000 and in its first year saved $61,500 in solvents and labor costs.
- Clean-up time for a tank was reduced from three hours and one operator to 10 to 20 minutes plus five minutes of an operator's time to insert the spray head. The new system also does a more thorough cleaning job than was done manually.
- Reduced down time for tank cleaning meant improved productivity.
- Employee safety and comfort were improved by eliminating tank entry.

The Idea Team

The technical employees who conceived and implemented the new tank cleaning method:

Manfred Haak
Manufacturing,
Hilden, West Germany

Klaus Schmehl
Engineering,
Neuss, West Germany

5861M

Environmental Engineering and Pollution Control Dept./3M
P.O. Box 33331, Bldg. 21-2W
Saint Paul, Minnesota 55133
(612) 778-4791

3M

Source: 3M Corporation

The Emerson Electric Company developed a chemical waste management program on the initiative of its Special Products Division and with the support of the president and vice president. In addition to having addressed several immediate waste management concerns, the program seeks to 1) eliminate unauthorized dumping of spent chemicals, 2) educate employees on the proper disposition of waste chemicals, 3) prevent chemical spills, and 4) comply with environmental laws and regulations. Through its waste management program, Emerson has been able to adjust its effluents to conform to effluent guidelines, to reduce its downtime, and to implement various pollution reduction measures with a maximum payback period of 2 years for a single project.

Environmental Auditing

Environmental audits are efforts to improve environmental quality management and to check environmental performance (NCPPP 1985). Specifically, an environmental audit is "a thorough examination and testing of a company's or facility's operating records and environmental practices, to gather information about its compliance with federal, state, and local environmental regulatory requirements" (Russell 1985). Environmental auditing differs from monitoring in that auditing actively seeks to ensure the effectiveness of a company's environmental activities, only one of which may be effluent data collection through monitoring.

There are two types of environmental audits: a) those carried out by firms themselves, using their own employees or outside contractors, or b) those imposed by regulatory agencies. Audits originating in-house fall within the context of good operating measures. Firms typically conduct audits to determine their own regulatory compliance and thereby avoid fines, but can also use the information to formulate expenditure and operating budgets and to search for ways to reduce hazardous waste and its associated costs.

The size and composition of an internal audit team depends upon the resources available to the company, the size of the waste problem, the objective of the audit, and other similar factors. Since auditing can be a legal procedure, the team ideally could include an attorney and a Certified Public Accountant who can advise technical and supervisory personnel on liabilities resulting from audits and on tax and financial issues. The team should also include at least one engineer knowledgeable of plant

operations and another who is familiar with industry practices and environmental regulations. If a component of the audit is problem rectification, then more engineers may be included: an environmental department representative, a principal design engineer, a facilities engineer, a process engineer, an instrument/control engineer, etc.

Auditing procedures can vary according to what the firm wishes to accomplish with it. A sample step-by-step procedure for audit preparation and performance might be the following, (Conrad 1985):

1) Assemble pertinent documentation. Documentation of plant operations can include current operating instructions, piping and instrumentation diagrams, layout drawings, instrumentation logic, maintenance and preventive maintenance records, environmental incident reports and emergency procedures. Documents on audit procedures may include outlines for interviews with operating personnel, check lists, manuals, and/or other working papers.

2) Conduct an environmental process review. An environmental process review is an analysis of the plant's design and operation for current or potential points which can generate process wastes. The analysis can include an evaluation of the process raw materials, the process equipment, the way in which the equipment is integrated into the overall facility, and other process-related concerns.

3) Conduct a procedure evaluation. Using the documentation on operating procedures, a check is done to ensure that the plant is operated as designed. The process procedures must also correspond to the process instrumentation logic, which describes the action of valves, instruments, and interlocks, and identifies switch points, alarm points, and fail-safe points. Evaluation of material handling and warehousing procedures should reveal practices which have waste-generating potential.

4) Carry out a site inspection. Questions that have arisen during the process review and procedure evaluation can be answered during the site inspection. The inspection permits an assessment of the accidental spill/leak

potential in the physical dimensions of the storage, process, and effluent collection areas of the site. Other practices can also be evaluated.

5) Report on and follow-up the findings. The report emanating from an environmental audit lists the personnel interviewed, the probable impacts of each problem, recommendations on solutions, and the cost outlay/savings estimates for each solution. Follow-up meetings of the team are held to ensure action on recommendations.

Some examples of problems frequently encountered in an audit are given in Table 2-1.

Through environmental audits, firms can rectify problems before being forced to do so by regulatory agencies. This helps to avoid compliance costs and fines for violations. Moreover, auditing can increase a firm's efficiency and profitability by:

1) Spotting opportunities to reduce waste and, therefore, disposal costs.

2) Lessening the likelihood of an environmental accident.

3) Compiling environmental cost information for financial purposes.

4) Teaching employees to be alert to environmental requirements and the cost of materials lost through poor practices and carelessness.

These are some of the obvious benefits of implementing the practice of environmental auditing. Audits can also lower the potential for lawsuit, improve public relations, protect investments in pollution control equipment, and keep environmental insurance rates low, all of which add up to substantial long-term cost savings. The official EPA policy position encourages environmental audits, but also states that "...auditing should remain a voluntary activity" and that "EPA will not routinely request environmental audit reports." (Federal Register 1985).

Waste Reduction Audits

The concept of waste reduction audits is quite new. This type of audit differs from the conventional environmental audit in one key aspect: the regulatory compliance is

TABLE 2-1 SOME FREQUENT PROBLEMS ENCOUNTERED BY AUDITORS

WATER

- Process discharges to the storm sewer
- Inoperative or poorly maintained sampling equipment
- No effluent flow-measurement device
- Process-area diking broken or nonexistent
- Storm drains in liquid bulk-transfer areas
- Oil-water separators improperly installed
- No laboratory quality-control/quality-assurance program
- Runoff from storage piles going to the storm sewer
- Improper permit reporting
- Outdated or poorly written Spill Control Plan

AIR

- Vents and exhausts not registered
- Lack of data on registered or unregistered emission points
- Lack of Air Pollution Episode Alert Plan
- "Guesstimates" on performance of control equipment - lack of test data
- Improper worker protection in dusty environment
- Neighborhood complaint file incomplete and/or lacking resolution of complaints
- Dust from plant operations on building roof and pavement

SOLID WASTE

- Sloppy housekeeping
- Careless drum or container handling (leaks and/or dents)
- Mixing process waste with office trash
- Unreported in-plant dumpsites
- Poor recordkeeping
- Incomplete analysis of hazardous wastes being sent offsite
- Incomplete files on past disposal practices
- Unlabeled drums
- Leaking containers

Source: Managing Your Environmental Audit (Russell 1985).

not addressed. The main objective of the waste audit is to identify options which have a potential of minimizing waste generation.

Preferably, the audits should be conducted by experienced engineering and operations personnel not directly involved with the audited facility. The waste audit counsists of nine steps (Fromm and Callahan 1985):

1. selection of the audit team
2. compilation of a waste stream list
3. generation of waste reduction options
4. ranking of options
5. preparation of documentation in support of options
6. joint review of options with plant personnel
7. analysis of revised rankings
8. final selection of options for further study and audit report preparation

The options selected through the audit activities may then undergo detailed technical and economic feasibility evaluations, if required.

Environmental/Safety Reviews of Operations

Periodic environmental/safety reviews of operations are necessary to ensure that a company's hazardous substances management and control system remains abreast of modifications in plant operations and of developments in hazardous substances management technology. This is important both for worker health and safety and for environmental compliance and waste reduction.

The National Agricultural Chemicals Association recommends regular meetings of supervisory personnel on the subject of safety and health rules (NACA 1981a, 1981b). These meetings are held to evaluate current rules and to formulate new procedures which reflect changes in operations. The review procedure itself is carried out in conjunction with a program of employee drills and safety meetings covering a range of hazardous substance handling topics.

An example of an environmental safety review program is the Toxic Chemicals Review Committee of West Point Pepperell, a textile manufacturer with 22,000 employees and 40 manufacturing facilities in eight states (Huisingh et al 1985). On the impetus of a suggestion by the Director of the Medical Department, the committee was formed in 1978 and contained the following personnel:

- An industrial hygienist.
- Three research chemists.
- A professional engineer.
- A corporate attorney.
- A corporate safety officer.
- A chemical production representative.
- A corporate information specialist.

The committee began reviews in 1976 of chemicals in current use and of chemicals proposed for use. It based its analysis of each chemical on the following criteria:

- Personnel safety considerations.
- Fire hazard potential.
- Hazardous properties (ignitability, toxicity, corrosivity, reactivity).
- Availability of less hazardous alternatives.
- Biodegradability.
- Heavy metal content.
- Potential for accumulation in the facility.
- Potential for release to the environment.
- Hazard potential when reacted or mixed with other chemicals.
- Proposed manner of use.
- Ultimate destination of the chemical.
- Hazard potential to the consumer.

Since 1976, the company has rejected or substituted a number of chemicals deemed inappropriate for its operations. Procedures were established for the purchasing of chemicals so that a share of the burden of reviewing chemicals could be passed on to the individual manufacturing operations. All chemical purchases may be made only on approval by the Corporate Research Chemist, who follows committee guidelines.

A large part of the waste reduction or waste prevention at West Point Pepperell has come about by replacing hazardous chemicals with safer ones and by preventing hazardous chemicals from being brought into use in the first place. West Point Pepperell now generates only a small amount of solvent waste which is sent off-site to a refining company.

Environmental/safety reviews of operations can be conducted at low cost depending on the size of a company's hazardous materials problem, the amount of in-house resources that can be committed to the effort, and other similar considerations. A review procedure can be used in conjunction with safety audits to preserve worker health, and/or with environmental audits for ensuring compliance with environmental regulations. The potential benefits from adopting this procedure are therefore significant. In fact, "The best type of audit for assuring environmental compliance is not really an audit at all, but a continual review of operations by plant management and personnel" (Russell 1985). A formal audit is then conducted occasionally to verify progress.

2.2.2 Employee Training

An effective "good operating" campaign to reduce the amount of hazardous waste generated in-plant must incorporate an employee training program. The personnel responsible for operating and monitoring process equipment, for off- and on-loading hazardous materials, for storing and transfering toxic substances during plant operations, and for similar and related tasks, need to be trained to adhere to safe operating procedures, proper equipment use recommendations, correct process control specifications, and good industrial hygienic practices. A sound policy of keeping employees informed of proper practices and of rectifying abuses contributes greatly to the protection of worker health, plant facilities, and the environment.

According to recommendations made by the National Agricultural Chemicals Association, the training of employees in safe hazardous materials handling should take place in three stages: 1) prior to job assignment, 2) during on-the-job training, and 3) ongoing during the employee's tenure with the company (NACA 1981b). Prior to assuming a position, an employee should be given a review of the types of materials to be handled, including their toxic properties, the health consequences if exposed, and any byproducts resulting from fire or explosion. The care and fit of any protective equipment required should also be covered.

When the employee begins working, the focus should turn to the safe operation of equipment and proper materials handling and spill cleanup procedures. Techniques are demonstrated for minimizing the amount of material allowed to escape and the human exposure to it. Employees are also taught the signs and methods of detecting the release of toxic material into the work environment.

Ongoing training should consist of regularly scheduled drills and safety meetings in conjunction with supervisory reviews of industrial hygiene, materials handling, and emergency practices. In this manner, the procedures in effect always correspond to the chemicals and equipment in use.

2.3 Procedural Measures

2.3.1 Documentation

Documentation of process procedures in a manual or set of guidelines ensures that job duties are precisely defined. This is especially important in an integrated production process where unsatisfactory performance during one step can adversely affect the remaining steps of the process. In general, a well-written operating manual or set of instructions (Stus 1984):

- Informs the employee how his job fits into the overall process.
- Describes startup and shutdown procedures, normal operations procedures, emergency procedures, and special procedures.
- Identifies important control parameters, including target emission or effluent levels.
- Defines operator's job responsibilities.
- Describes potential personnel hazards.

This information is necessary if an employee is to operate equipment safely and economically. Ideally, the topic of environmental control should be given separate

treatment. The employee should be made aware of controlled versus uncontrolled waste generation rates, the target rates for the process, and the consequences to the organization of not meeting the targeted rates. In addition, effluent sampling procedures and control equipment failure procedures should be outlined. Adherence to procedures and use of the information provided can contribute to reduced waste generation.

Process documentation of this type also promotes product consistency, lessening the likelihood of producing unacceptable product which must be discarded. Moreover, procedural guidelines can be helpful in reducing waste generation during maintenance or emergency shutdowns.

Material safety data sheets (Form OSHA 20) are prescribed for hazardous materials by the Occupational Safety and Health Administration of the Department of Labor. Although intended primarily as a safety precaution, the material safety data sheets (MSDS) can aid in reducing hazardous waste generation. These sheets contain the manufacturer's information on the chemical, physical, and toxicological properties of the hazardous substances being used; they also contain recommendations on the proper handling and storage procedures for these substances. Following these recommendations reduces the likelihood of spills and of waste creation due to cross-contamination with other chemicals. In the event of a spill, a response crew can refer to the appropriate MSDS for instructions on how to clean up the chemical while producing the least hazardous waste.

Consolidated Diesel of Whitakers, N.C., uses material safety data sheets to screen all hazardous materials coming into the plant (Kohl et al. 1984). The company routes MSDSs through hazardous material and medical personnel during the requisition process. The approval of these individuals is required before a substance is allowed onto the plant site. This ensures that each substance is properly documented and evaluated in terms of its hazardous characteristics prior to its use. This can reduce hazardous waste generation by preventing the use of some materials which would require regulated disposal.

In addition to having material safety data sheets, each substance should be stored and handled in containers that are clearly marked with information on contents, storage

and handling reommendations, spill procedures, and requisite first aid for exposure. Some innovative products have recently been developed to aid in labeling. The Legitronic 2060 electronic labeling system, manufactured by Weber Marking Systems of Arlington Heights, Illinois, prints labels on an as-needed basis which contain information on product identification, weight, lot number, health hazard warnings, first aid and spill procedures, and storage and handling instructions. The labels can contain Department of Transportation symbols when needed. The system is in use at Stephan Company of Northfield, Illinois, where 400 separate products are produced at four separate production facilities (Bobrowicz and Powers 1985).

Another labeling method rapidly coming into use is the automatic identification system using bar codes (Powers 1985). Bar coded labels can link containers and materials to a computer through the production, inventory, storage, and shipping stages. This improves the accuracy of material tracking and inventory accounting, thereby allowing work-in-process monitoring and preventing material from going astray on the plant site and/or becoming dated. Hazardous waste in the form of discarded chemicals and waste resulting from inefficient operations are reduced in this manner.

2.3.2 Material Handling and Storage

Most processes involve the storage of raw materials, products, and wastes and the transfer of these items from one area of the plant to another. Proper materials handling and storage ensures that raw materials reach the production process without spills, leaks or other types of losses which could result in waste generation. Similarly, proper materials handling ensures that products and wastes which result from the production process are transferred to off-site locations without additional waste generation.

There are strong economic incentives for firms to handle and store materials properly. Losses from improper handling and storage can often be curtailed without incurring large capital costs (e.g. by changing procedures or organization). Thus, firms tend to employ proper materials handling procedures because it is profitable to do so. The proper storage of hazardous materials includes:

- Adequately spacing rows of drums to allow for a visual inspection of each container for corrosion and leaks.

- Stacking containers no higher than recommended by the manufacturer and in such a way as to minimize the chance of tipping, tearing, puncturing, or breaking.

- Refraining from stacking equipment against containers.

- Maintaining distance between different types of chemicals to prevent cross-contamination.

- Providing adequate lighting in all areas where hazardous substances are stored.

- Insulating electrical circuitry and checking it frequently for corrosion and potential sparking.

- Keeping aisles clear of obstructions.

- Maintaining a clean, even surface in areas trafficked by personnel and equipment.

- Raising drums off the storage area floor to prevent corrosion through concrete "sweating".

- Curbing or diking around process storage tanks/area.

In addition, using larger containers for chemical storage reduces the ratio of container surface area to volume, implying less cleaning waste per unit of volume stored. Larger containers also obviate the need to handle wastes in 55-gallon drums, which themselves can become hazardous waste and are unsafe and inconvenient. An example of an alternative to 55-gallon drums would be polyethylene containers enclosed in rigid wire mesh. These can be constructed to hold up to 6 times the capacity of a 55-gallon

drum. The containers are portable, reusable, and can be outfitted for top or bottom discharge, cleaning access, locking, and easy trucking.

2.3.3 Material Tracking and Inventory Control

Accurate material, product, and waste tracking provide operations supervisors with information on the inventories of hazardous chemicals at each location on the plant site. This enhances the development of a materials handling and storage procedure which avoids hazards. Also, the availability of information on the quantities of waste being generated from discarding unused chemicals may contribute to concerned management setting a waste reduction program in motion.

Computers are increasingly being used in industry to monitor inventories and track materials through processes. Material tracking computer software is available which can list the names and locations of all hazardous materials on site in addition to maintaining environmental monitoring, employee health, and chemical exposure information (Giltenan 1984). Process control equipment allows process specifications to be controlled using sensors; when undesired changes occur, corrections are sent to control instruments. This reduces the number of discards by increasing the quantity of product on-specificaton. Also, the electronic bar code labelling systems mentioned above allow information on a container's contents to be read by lasers into computers. The bar codes enable continuous monitoring of inventories.

2.3.4 Scheduling

Timing often plays an important role in the production of waste generating products. It has a special significance in batch production operations, where equipment cleanup waste volumes are directly related to cleaning frequency. To reduce cleaning frequency, it is necessary to maximize batch size and equipment dedication to a single product. This requires good scheduling and planning. The reader is further referred to the study of process equipment cleaning in the appendix.

2.4 Loss Prevention Practices

2.4.1 Spill Prevention

The spillage of a hazardous chemical results in hazardous waste. Washdowns of spilled toxic chemicals create liquid hazardous wastes which are subsequently transferred off-site for disposal. Mopups using absorbent materials create hazardous solid waste which must also be disposed of. To minimize the costs incurred in chemical spill incidents -- which can be a range of costs from disposal fees and employee care to fines from enforcement actions -- the best practice is to prevent spills from occurring in the first place.

The likelihood of a spill can be lessened by 1) conducting hazard assessment studies at appropriate points in the design and operation phases, 2) using properly designed storage tanks and process vessels only for their intended purposes, 3) equipping all such containers with overflow alarms, 4) testing the alarms periodically, 5) maintaining the physical integrity of the containers over time, 6) setting up administrative controls for all loading/unloading and transfer operations, 7) installing sufficient secondary containment facilities, 8) having a good valve layout, 9) having interlock devices to stop flow to leaking sections, 10) disallowing the operators to bypass the interlock or to alter the set points, 11) isolating equipment or process lines that are not in service, and 12) documenting the spillages and related dollar values (Kletz 1982, Sarokin 1985). These measures can be implemented through a spill prevention program that provides input into plant design as well as the administration of plant operations.

Hazard assessment studies are best performed during the conceptual design, the design-freeze, the prestartup, and the operational phases of a plant (Ozog 1985). Moving from the design to the operation phases, hazards become easier to detect, but changes in the process become more costly since the financial commitments to a set process design are in place. During the conceptual design phase, the focus is on hazards which affect the general public and the environment, including the release of chemicals, explosions, and fugitive emissions. The chemicals involved in the process are identified by their physical, chemical, and toxicological properties, and it is determined whether special handling, monitoring, and/or control is required. Also at this time, a separate study team is put together to compile a list of events which could

credibly lead to hazards. A consequence analysis is done for each event, out of which a set of recommendations for precautionary measures emerges.

The design-freeze phase is that interlude between the completion of the piping and instrumentation diagrams and the determination of operating procedures. For new facilities, a full hazard and risk assessment should be performed here. A comprehensive effort could encompass (Ozog 1985):

1) Definition of scope.
2) Collection of data.
3) HAZOP study of entire facility.
4) Qualitative ranking of hazards.
5) Quantitative analysis of selected hazards.
6) Integration of hazard probability and impact estimates.
7) Risk comparison.
8) Evaluation of risk-mitigation measures.

At this point, alterations in process design still can be made relatively inexpensively since equipment has not yet been ordered.

Prior to starting up the process, a final check should be done to verify the status of recommended changes that emerged from the hazard and risk assessment. A site inspection should be conducted to form an impression of spatial dimensions, and the hazard and risk assessments should be brought up-to-date. Design changes at this point are expensive.

Shortly after startup, operating procedures may be revised, and these revisions should be reviewed in the context of the hazard and risk assessments. Also, changes in the process may be made during the operational life of the plant; these changes should be similarly reviewed under further hazard and risk assessments. Assessments should be carried out regularly during the operational life of the plant.

Sound practice dictates that storage tanks and process vessels containing hazardous chemicals be properly designed and used only for their intended purpose. They should also have, as a minimum, overflow alarms. Once these conditions are met, it remains

to ensure the structural soundness of the containers, to enforce proper hazardous materials handling procedures, and to construct and maintain secondary containment and collection facilities (Shields 1980).

The structural soundness of the tanks and vessels can be assured through an inspection and record-keeping initiative. Monthly visual inspection of tanks, including all equipment connected to them, the tank's seams, and the supporting structures, should be conducted. Physical inspection and testing should take place at the half-life of each tank, or more frequently if the tank materials are subject to attack by the chemicals in the tank. Discharges from internal heating and cooling coils should be monitored and tested at least quarterly. All these efforts can be conducted in coordination with other existing safety and operating checks.

Spills are most likely to occur during loading/unloading operations and in-plant transfer activities. For this reason, written procedures should be kept current and made easily accessible to all employees. In addition, a spill response plan should be formulated, and employees should be trained both in the current operating procedures and in the correct implementation of emergency spill measures. A policy of taking disciplinary action on violations, if strictly enforced, can ensure employee adherence to procedure.

An effective spill prevention program will carry over into the design phase of plant operations. In structuring a production/storage facility, equipment should be designed or ordered which, by its construction, does not allow hazardous substances to leak from the process. The variations on equipment types and designs are numerous. Successful applications have been double mechanical seals, rupture disk-relief valve combinations, seal welded or all welded piping construction, flange guards, and bellow-sealed valves, to name only a few. Some case examples of spill prevention measures through equipment designs and facilities repairs are given below.

Sealless pumps - In modernizing its benzene facility in 1977, a major oil company selected a sealless-type pump for its benzene transfer operations. The design prevents leakage and subsequent exposure of workers and the environment to EPA-regulated chemicals (Suzuki 1985).

Interlock devices - In some installations, filtration units are generally washed with hot water and the wash liquid allowed to run into a drain through a drain valve. If by mistake the drain valve is left open when the filter is put back in normal operation, the filtrate liquor will drain out resulting in a spill. By installing an interlock device that stops feed to the filter when the drain valve is open, such spills can be prevented (Kletz 1982).

Bellow-seal valves - The design of these valves relies on the use of hermetically sealed bellows (torsional or compression type) which connect the valve body to its moveable stem. The design is preferable to a standard packing-type seal for highly hazardous, flammable, or corrosive services.

2.4.2 Preventive and Corrective Maintenance

Maintenance programs, whether preventive, corrective, or a combination of both, can prove instrumental in cutting production costs stemming from expensive repairs, excessive waste disposal, and business interruptions. They can also prevent hazardous waste releases due to equipment failure and facilities degradation. These programs have difficulty, however, in gaining the acceptance and support of upper management.

Preventive maintenance planned to minimize equipment breakdown and malfunction is a major part of an overall maintenance program, as losses for this reason can account for three to four times the level of operating and maintenance costs (Rimberg 1980). Despite this fact, preventive maintenance is often viewed or perceived, as an expenditure which does little, if anything, to improve efficiency and profits. For extensive maintenance programs to be adopted, it must be quantitatively demonstrated that a particular program can result in 1) cost reductions, 2) cost avoidance, and 3) a good return on the investment.

To demonstrate these points, measurements must be taken of maintenance labor productivity and management, planning, and scheduling effectiveness. Indices can be devised to measure how well a maintenance program is working. An index of labor productivity is the ratio of work order process time to time needed to complete maintenance tasks, for example. A maintenance control index, which is a measure of management effectiveness, can include (Rimberg 1980):

1) The current backlog of work orders.
2) The backlog of maintenance manhours.
3) The number of open work orders.
4) The number of hours assigned for work in a specific area.

Indicators of the results of maintenance planning can be (Rimberg 1980):

1) Jobs finished on time.
2) Forecasting accuracy.
3) Maintenance hours planned vs. hours worked.
4) The amount of emergency work.
5) The amount of overtime.
6) The amount of equipment downtime.

The performance of a maintenance program can be determined by assessing (Rimberg 1980):

1) Productively employed maintenance manpower.
2) The effectiveness of maintenance while a plant is in operation.
3) The ratio of maintenance labor to maintenance materials costs.
4) The ratio of maintenance cost to unit of product.
5) The ratio of maintenance personnel to total plant personnel.

Careful recording of these measurements can reveal the value of a maintenance program. The following example of air pollution control equipment maintenance serves to illustrate the above:

> "As an example of the need to measure maintenance performance, the following situation was encountered: A plant had 12 dust collectors of assorted sizes with 50 to 250 bags of the pulse jet and shaker types. All collectors were usually maintained on an emergency basis; that is when malfunction aborted production. In addition, the source was fined $25,000 by the state for continuous failure to comply with emissions regulations. Corporate management requested that plant management compute the costs incurred from loss of production and excessive baghouse component replacement (valves, bags, etc.). Loss of production

accounted for approximately $500,000 and baghouse repairs $50,000. Labor costs were extremely high, although not easily estimated, since the maintenance department did not assign task and job costs. In addition to these costs, excessive amounts of plant management time were being consumed handling regulatory matters. The major underlying problem in this situation was the lack of appropriate maintenance management procedures. Upon final evaluation of the economics of the situation, a contract preventive maintenance program was instituted. It should be noted that the most important step in initiating this activity was to persuade operations personnel that the program would make the process equipment more responsive to their needs. An expenditure of $36,000 was made to execute the program and after 1 year costs of malfunction and loss of production were reduced to $128,000. In-plant labor costs were also clearly defined and amounted to $32,000." (Rimberg 1980)

To illustrate a preventive maintenance program, the following is the required information to develop a program directed at mechanical equipment (Hellhake 1981):

1. A list of all plant equipment.
2. A knowledge of operating time for each item or area.
3. A knowledge of which items are critical to the process(es).
4. A knowledge of problem equipment.
5. Vendor maintenance manuals.
6. Manual or computerized repair histories.

A separate card or instruction sheet can be typed for each equipment item in the preventive maintenance program. These cards can be filed in a number of ways: 1) based on maintenance schedule (most frequently used), 2) based on plant area (useful if a plant section is down unexpectedly and one wants to do the maintenance in that area) or 3) based on specific equipment number.

Like effective spill prevention programs, an effective maintenance program carries back into the design phase. Designs should take into account the access of maintenance equipment and personnel to process equipment components and accessories. Design consideration should include larger access doors, wider internal catwalks, accessible components, hopper access doors, and duct cleanout and

inspection hatches. Specification of easily maintained equipment at the outset serves to reduce the cost of preventive and corrective maintenance during operation.

Preventive maintenance can be less expensive and more efficient in some cases if contracted out to a maintenance firm. Cost and efficiency advantages can be found in 1) the increased time that plant personnel can spend on production operations, 2) the easy handling of fluctuating workloads by contract maintenance firms, 3) the avoided expenditure on crews, repairs, repair facilities, tools, and measurement instruments, and 4) the greater operational experience of contract maintenance personnel, which leads to more rapid identification and troubleshooting of equipment malfunctions and thereby to product improvement. Also, the concern over environmental compliance can be placed to some degree on the contracting firm (Rimberg 1980).

2.4.3 Emergency Preparedness

Part of overall good operations resides in maintaining a state of emergency preparedness for chemical spills and/or fires. The exposure of both the plant's employees and the immediate environment to releases of hazardous or toxic chemicals can be minimized with a well-conceived emergency management procedure.

The Occupational Safety and Health Administration, by virtue of regulations published in the Federal Register (39 CFR 1910.1200, 48 FR 53280, November 25, 1983), requires chemical manufacturers and all plants using chemicals to implement a hazard communication procedure. The procedure should provide for the identification of the hazards of all chemicals produced and for the distribution of this information to chemical users and their employees. As management and employee awareness of hazards is the first step to preparedness, compliance with this regulation can form the informational basis for an effective emergency program.

The essential requirement of the regulation is that by May 25, 1986, all hazardous substances must be properly labeled with material safety data sheets (see Section 2.3.1) and all employees adequately trained in the handling of these substances. To meet the requirement, the following should be accomplished (Brown 1985):

- The OSHA standard should be reviewed and the extent of its applicability determined for the individual plant.

- Chemical users should list chemical substances used and obtain a material safety data sheet for each.

- Chemical manufacturers or importers should list all substances and determine the hazards of each.

- Employee hazard information and education procedures should be formulated and should include informing employees of the hazards of nonroutine tasks and educating outside contractors about on-site hazards.

Figure 2-4 describes a sample management program to comply with the regulation. It is important to note that as with any other successful organizational innovation, a commitment from management is the primary motivation for the change.

Using materials safety data sheets and an in-place employee training program, an emergency procedure can be developed. Emergency response preparation and procedure can vary greatly in detail, depending on the size and location of the plant (i.e. the potential size and spread of a spill), the number and toxicity of chemicals in use, and like factors. One organizational suggestion is to maintain a separate comprehensive dossier for each chemical (Berry 1980). Readily giving a complete technical report can serve two functions: 1) it can provide a measure of legal protection for the firm by being an indication of "good faith", and 2) it can prevent a small spill incident from evolving into a larger one due to incorrect cleanup procedures.

One portion of the chemical substance file can be a record of the data required for briefings of the media, emergency teams and regulatory personnel. These data should include (Berry 1980):

- Hazardous material classification (DOT).

FIGURE 2-4 SAMPLE PROCEDURE FOR OSHA COMPLIANCE

Corporate Management Commitment

Operating Unit Determines Policy and Establishes Position

Line Management Develops Program and Procedures and Directs Implementation

Regulation Applicability Determined

Input, Output, and Intermediate Chemicals Listed

Chemical Hazard of On-Site Production Determined

Material Safety Data Sheets and Labels Prepared and Assembled

Workplace Hazards Assessed

Protective Measures Established and Labels Installed

Information Program Written

Affected Personnel Trained

Source: Understanding and Complying with OSHA's Hazard Communication Regulation, (Brown 1985).

- Emergency service numbers (U.S. Coast Guard; state regulatory and response agencies; police, fire, and health departments; health care facilities; area water treatment plants; area health facilities; media outlets).

- Location and quantity of chemical spill, the route of entry into the human body, and the medium holding the chemical.

- Date and time of discovery, bodies of water affected, number of employees involved and extent of injuries, if any.

- Weather conditions, containment/removal actions, other chemicals present, and potential problems.

The remainder of the file can be comprised of specific information on the fugitive chemical and the remedial action (Berry 1980):

- Name, address, and phone of vendor (plus information on other vendors and consultants).

- Symptoms of exposure and recommended first aid.

- Fire protection measures.

- Environmental protection measures.

- Protective equipment required.

- Sampling and laboratory measurement methods.

- Details of training and education efforts for employees, health care personnel, law enforcement personnel, and the media.

Additional considerations must include such elements as community awareness programs, site emergency evacuation plans, site emergency services, and coordination of site emergency plans with surrounding facilities and local authorities.

If carefully acquired and kept up-to-date, this information can support capable hazardous spill management. Training employees in proper spill procedures and informing those capable of rendering assistance can also help to minimize human and environmental injury.

A good example of planning for agricultural chemical fire contingency is provided by the form distributed by the National Agricultural Chemicals Association. The form lists the information useful in the event of a chemical fire. For instance, the phone numbers of plant authorities, state agencies, and emergency personnel are kept on file. Sketches are made of the plant layout and vicinity areas as well as of the drainage likely to occur during liquid spills and washdowns. The owners and uses of surrounding areas are described, as are any local water supplies which might be affected or utilized. Finally, a record is kept of scheduled reviews or updates of the plan in order to keep the plan current.

3. OBSERVATIONS AND CONCLUSIONS

3.1 Process Characteristics and Good Operating Practices

The applicability of good operating practices is determined at the level of the individual plant or company. Two plants producing the same product may have different process or organizational structures which make a particular measure more or less applicable. For example, two plants using bar coded labels may realize different degrees of success in material tracking or inventory control depending on the routing of the materials through production operations, the care taken to ensure error-free data entry, etc. Nevertheless, certain process characteristics and economic conditions do appear to enhance the effectiveness and/or implementation of good operating measures.

In less automated plants, fewer automatic process controls are in place and the level of human involvement is higher. There is, therefore, greater room for human error in

equipment operation, material handling, inventory control, production scheduling, etc. Training programs and procedural reviews can thus have a greater effect in reducing waste generation from those activities. In more automated processes, there is not as much call for procedural refinements or training improvements.

At plants using highly toxic materials, the handling and storage of these materials tends to be more closely regulated both by government and by the firms themselves. Potential health hazards cause plant managers and personnel to track materials carefully, maintain equipment regularly, and react quickly and decisively in the event of a spill. Health and safety concerns at a plant producing epichlorohydrin, for example, typically would result in more rigor in implementing operating measures than do similar concerns at a paint-mixing plant.

Firms which use the same processing facilities for various products generally appear to have more potential to implement good operating practices. Producing a product mix implies a change of inputs and, perhaps, procedures for alternative product runs. In the production of product mixes, scheduling, material handling, supervision and training, and material tracking are not only more difficult but also more important in terms of maintaining throughput, minimizing leaks and spills, and finally minimizing waste generation. Moreover, there is generally more equipment cleaning as the equipment is prepared for the next product run. Sometimes it is possible to segregate the cleaning wastes by contaminant to allow for reuse and therefore produce a subsequent reduction in waste generation. The reader is referred to the process equipment cleaning study for additional information.

The foregoing observations suggest that greater potential for the implementation of good operating practices and the associated reductions of waste generation exists in batch processes rather than in continuous processes (except, perhaps, where batch processes use highly toxic chemicals such as in pesticide formulation). This is not to say that good operating practices are not important in continuous processes; on the contrary, preventive maintenance and spill prevention, for example, are essential considerations. Rather, batch processes are generally less automated, and have a higher degree of human involvement, coupled with a lower degree of equipment dedication to a single process medium in comparison to continuous processes.

Figures 3-1 and 3-2 present generic, block flow diagrams for batch and continuous processes. The line segments to the right show the range of individual process operations to which each good operating practice applies. Omitted are management initiatives and employee training which, as personnel measures, apply to the entire range of process activities. Documentation in the form of procedure manuals is omitted for the same reason.

3.2 Economic Aspects

Economic considerations suggest that plants which 1) use raw materials with lower unit costs, and 2) generate waste with lower unit disposal cost/remarketing value, are likely to have more waste reduction potential. Processes using raw materials with high unit costs, e.g. gold plating operations, will more readily have undergone modifications to recover lost values and/or improve the efficiency of input materials use. Similarly, plants generating wastes with high disposal costs relative to the revenue from the sale of the product will more readily have implemented good operating techniques. Good operating practices, such as waste stream segregation, will also be employed to purify and preserve wastes which can be marketed. In this case, disposal cost must meet or exceed the cost of containing the waste less the revenue received for it.

At the level of the individual firm, the available resources and the target compliance parameters (and their enforcement) determine the breadth and quality of the pollution abatement effort. Large generators, which generally have the necessary financial and personnel resources and which have been under regulation longer, have developed comprehensive environmental programs in an effort to reduce disposal costs and avoid fines stemming from non-compliance. While good operating practices are certainly in evidence in these companies, their environmental efforts include examining and implementing extensive process changes to reduce waste. Small generators, on the other hand, do not have large amounts of financial and personnel resources and are only now coming under regulation. Small firms can little afford the expense of investigating various pollution abatement methods, may not have the expertise to do so, and most likely could not withstand the losses from business interruption that the implementation of these methods may entail. For small generators, then, good operating practices offer more promise for waste reduction. Many of these practices can be instituted quickly with little or no capital investment and require merely an

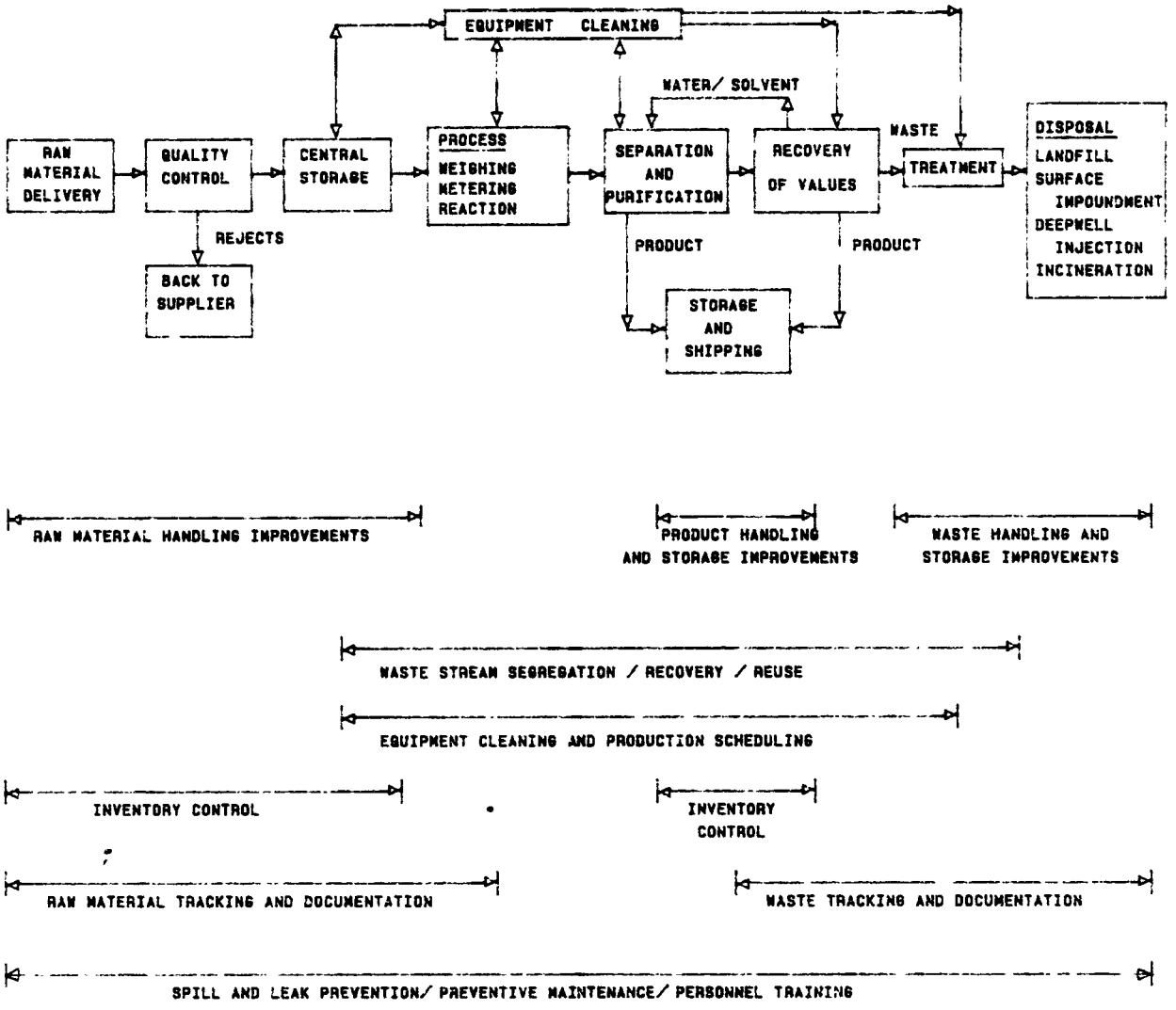


Figure 3-1 Generic Batch Process

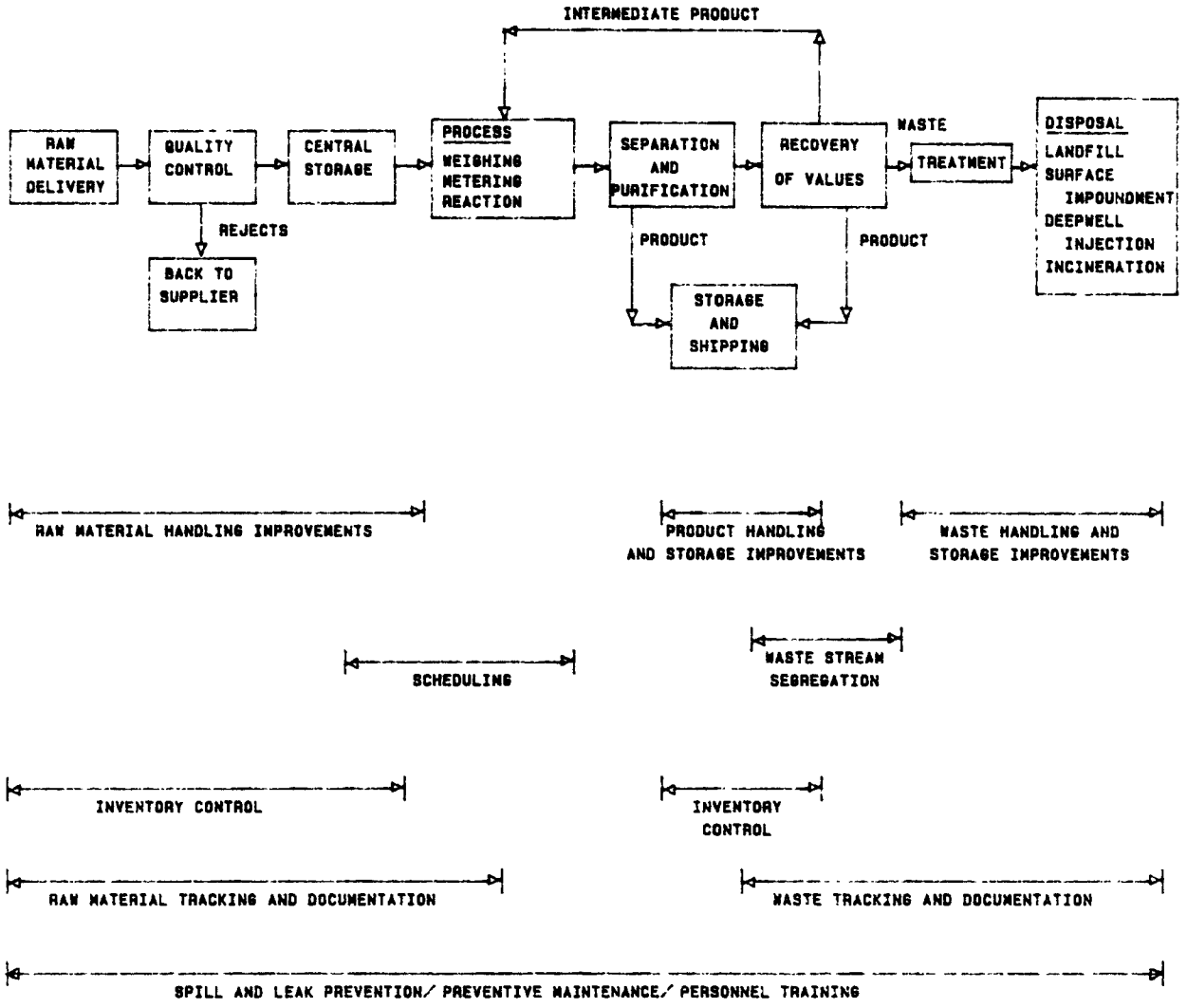


Figure 3-2 Generic Continuous Process

examination of existing procedures. Therefore the benefit/cost ratio is potentially very high.

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5. INDUSTRY CONTACTS

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1. PROCESS: METAL PARTS CLEANING
2. SIC CODE: XXXX
3. INDUSTRY DESCRIPTION

Metal parts cleaning is an integral processing operation used by industries involved in the manufacturing, repair, and maintenance of metal parts and equipment. The major industries that practice metal parts cleaning are:

SIC Code	Manufacturing
2500	Metal Furniture
3300	Primary Metals
3400	Fabricated Products
3500	Nonelectric Machinery
3600	Electric Equipment
3700	Transportation Equipment
3800	Instruments and Clocks
3900	Miscellaneous

SIC Code	Service
4010	Railroad
4580	Air Transport
7530	Auto Repair

It has been estimated that the above listed industries consist of approximately 336,000 plants (USEPA 1979). Since not all plants employ metal parts cleaning operations, and since there is no direct connection between the size of the plant and the amount of cleaning being performed, no additional industry information is available.

4. PRODUCTS AND THEIR USES

Due to the diversity of the industries utilizing metal parts cleaning, a comprehensive listing of all products requiring cleaning would be beyond the scope of this report. Virtually all fabricated metal objects require some form of cleaning.

5. RAW MATERIALS

There are basically five different types of cleaning media employed by industry. The five types are nonchemical (or abrasives), solvents (halogenated and nonhalogenated),

alkalines, acids, and water. Alkaline and acid cleaners are usually referred to as aqueous cleaners. A sixth type, emulsion cleaners, is a mixture of nonhalogenated solvent and alkaline cleaner and is therefore not considered separately. Table 5-1 presents a breakdown of cleaning media usage (excluding water) by overall U.S. market share.

Table 5-1 Raw Materials Used for Metal Parts Cleaning in 1981

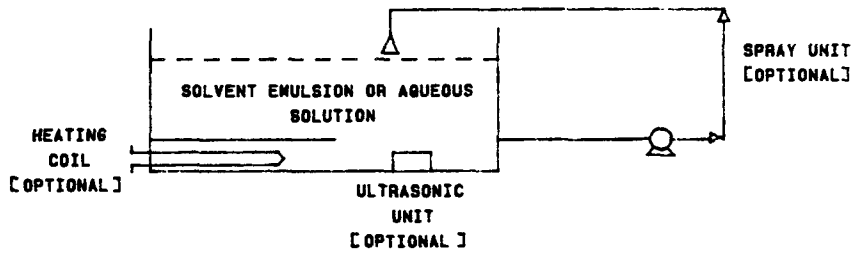
Materials	Market Share
Nonchemical	
Aluminum oxide	3%
Silicon carbide	
Silica	
Binder (grease, oil, or water)	
Halogenated Solvents	34%
Methylene chloride	
Perchloroethylene	
1,1,1-trichloroethane	
Trichloroethylene	
Nonhalogenated Solvents	24%
Aliphatic hydrocarbons	
Aromatic hydrocarbons	
Ketones	
Alcohols	
Aqueous	39%
Alkaline (alkaline salts plus deflocculants, inhibitors, and surfactants)	
Acid (sulfuric, hydrochloric, nitric, phosphoric, etc.)	

Source: Estimation of Market Share of Metal Cleaning Techniques (O'Brien 1981).

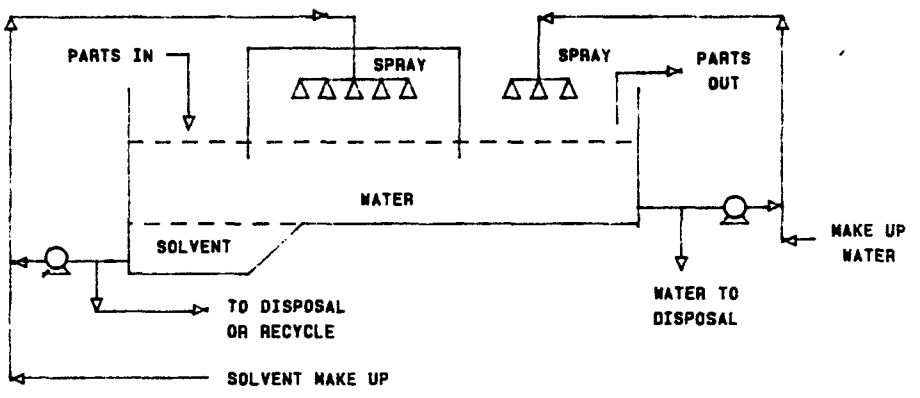
6. PROCESS DESCRIPTION

Detailed process descriptions of metal parts cleaning operations can be found in the open literature (Durney 1984). The following discussion presents a general overview of the operations involved. A process flow diagram of the major equipment items used for metal parts cleaning is shown in Figure 6-1.

SOAK TANK



DIPHASE SYSTEM



VAPOR PHASE SYSTEM

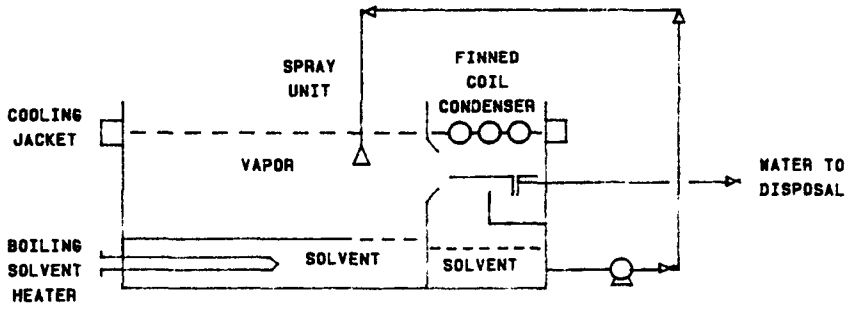


Figure 6-1 Metal Parts Cleaning Equipment

The discussion below excludes paint stripping which is covered separately in the study of paint application (B21).

Although most people think of metal parts cleaning as a very simple operation (such as washing an oily part in a tank of solvent), many parts require quite complex arrangements of several different cleaning operations. The sequencing of these various cleaning operations usually depend on three main interrelated factors. These factors are:

- The nature of the contamination.
  Not only is the composition of the contaminant important but also its history. For example, subjecting the part to heat (or other cleaning methods) can alter the physical properties of contaminants. Many times parts are contaminated with several different materials so that careful consideration must be made regarding the cleaning methods to be employed and their sequencing.

- The metal to be cleaned.
  The selected process should perform the cleaning to the required degree without adversely affecting the metal substrate. Since reactivity of metal with alkalis and acids varies, cleaners for one type of metal can be entirely inappropriate for another type.

- The required degree of cleanliness.
  The required degree of surface cleaning varies with application. For example, when parts are going to be cyanide zinc plated, critical cleaning is not usually required. This is because cyanide based plating solutions exhibit a strong cleaning action of their own and are very tolerant with respect to the initial degree of surface cleanliness. On the other hand, nickel plating requires a very clean substrate surface for nickel to adhere resulting in more thorough and rigorous cleaning of the part.

Even after careful consideration of the above factors, no one particular cleaning method can be readily specified. More commonly, several methods appear appropriate and they all require experimental, evaluation.

The five major classifications of cleaners used by industry are abrasives, solvents, alkalines, acids, and water. Cleaners (except abrasives) are normally held in large open tanks, with the parts to be cleaned mounted on racks or held in perforated horizontal barrels. The decision to use racks or barrels usually depends on the size and shape of the part and the type of coating required.

Abrasives are designed to remove rust, oxides, and burrs and create a smooth surface. Common abrasives are aluminum oxide or silicon carbide mixed with an oil or water-based binder. This material is applied to a buffing wheel (usually made from an absorbent material such as cloth), and then the metal part is held against the spinning wheel. The speed of the wheel is determined by the type of metal being buffed and whether the system is manual or automatic. Generally, manual systems run at lower speeds and are considered to be less efficient. Automatic systems, while being more efficient, generate more heat due to the higher speeds and can cause an oil-based binder to burn. This, in turn, leads to more difficult cleaning in subsequent stages. Another abrasive cleaning method, vibratory finishing, consists of a container that vibrates an entire load of metal parts in a bed of abrasive material and water. Other mechanical abrasive cleaning methods consist of tumbling barrels, centrifugal barrel finishing, centrifugal disc finishing, and spin finishing.

Solvents, the most widely used class of cleaners, are used for removing oil-based contaminants. Solvent usage is generally divided into three main categories or operations. These are:

- o cold cleaning
- o diphase cleaning
- o vapor phase cleaning.

Cold cleaning, which generally uses unheated or slightly heated nonhalogenated solvents, is the most common cleaning method. It was estimated that over one million cold cleaners are in operation, with more than 50 percent being used by the auto repair industry (USEPA 1979). The second most common solvent cleaning method is vapor degreasing. It was estimated that there were approximately 47,000 vapor degreasers in operation (89 percent open top and 11 percent conveyorized) (USEPA 1979). Vapor degreasers typically use a halogenated solvent vapor to dissolve oil-based

contaminants and the subsequent condensation of the vapor rinses the part clean. The final system, diphase cleaning, is similar to the cold cleaning soak tank method except that a water layer is floated on top of the solvent and provides for additional part cleaning. All of the methods mentioned above are described in the following paragraphs.

Cold cleaning operations can be divided into four distinct types of cleaning systems or methods. The first method, wipe cleaning, consists of soaking a clean rag with solvent and then wiping the metal part clean. This operation is strictly manual and the overall efficiency is low. Rags must be replaced frequently or the parts will not be properly cleaned. Another disadvantage of wipe cleaning is that the rags can leave lint on the part.

The second cold cleaning method, soak cleaning, consists of soaking the parts in a tank of solvent. Small parts are usually placed in a basket while larger parts are placed on a rack. Sometimes a small pump and spray unit are installed on the tank so that the parts can be more thoroughly cleaned. When soil contaminants are present (in addition to oil-based contaminants), emulsion cleaners can be used. Emulsion cleaners typically consist of five percent solvent, ninety-five percent water or alkaline cleaning solution, and various surfactants. The main advantages of emulsion cleaners over solvents are that they cost less and produce less air pollution. In addition, emulsion cleaners leave a slight oil film on the cleaned parts. This can be an advantage if the part is going to be stored for some time (the oil film provides rust protection), or a disadvantage if the part is going to be immediately electroplated (additional cleaning steps would be required to remove the oil film).

A third cold cleaning operation, ultrasonic cleaning, is identical to soak cleaning, except for the addition of an ultrasonic unit in the tank. When ultrasonic waves pass through a liquid media, cavitation occurs. Small vacuum bubbles are created which almost immediately collapse. The rapid implosion of these bubbles provides a vigorous cleaning action throughout the tank. Since this action occurs everywhere in the tank, ultrasonic cleaning is useful for cleaning parts with difficult to reach surfaces or crevices.

The fourth cold cleaning method, steam gun stripping, is used primarily for the removal of paint from a metal part or object. Stripper (a mixture of nonhalogenated solvents), is fed into the steam line through a valve and hose arrangement connected to the stripper storage tank. After the part has been stripped of paint, the valve is closed and pure steam is used to rinse the part clean.

Diphase cleaning systems make use of the fact that halogenated solvents are relatively insoluble in water. Therefore, solvent cleaning and water washing can be performed in the same tank quite easily. Parts to be cleaned first pass through a water bath, then a solvent spray, and finally a water bath and spray (see Figure 6-1). Solvent used to spray clean the part drops into the tank of water and sinks to the bottom. The solvent runs to the deep end of the slopped tank bottom and can be pumped back up to the spray unit. Since the unit is fully automated, and the solvent spray portion is fully enclosed, very little solvent loss to the atmosphere occurs.

Vapor phase cleaning, or vapor degreasing systems consist of a tank of halogenated solvent heated to the solvent's boiling point. Parts to be cleaned are placed in the vapor zone so that the condensing solvent dissolves the oil-based contamination and rinses the part clean. When the temperature of the part finally reaches the temperature of the solvent, condensation ceases and the parts can be removed dry. Since the potential exists for much greater air emissions than from cold cleaning dip or soak tanks, special recovery equipment is installed on the tank. The first item, a cooling jacket, is usually placed around the outside of the tank and is located at the vapor/air interface. By cooling the air above the vapor, a cool air blanket is formed which helps suppress vapor from escaping. A second unit, a finned coil condenser, is installed inside the tank and is designed to fully condense any vapor that reaches the coil. This condensate, which includes water evaporated from the parts and water condensed from the air (this water forms frost on the coil and is removed during the coils' defrost cycle), flows into a solvent/water separator. The separated water is sent to the facility's wastewater system and the solvent flows into a sump to be used by the cleaning tank spray unit. Vapor phase degreasers can be manual (open top) or conveyorized (fully enclosed).

Alkaline and acid cleaners, more commonly called aqueous cleaners, both utilize the same equipment and are therefore discussed together. Alkaline cleaners are used

primarily to remove soil from metal parts. Acid cleaners are used to remove rust, scale, and smut (formed when parts are electrocleaned). Recently, very strong alkaline cleaners (with cyanide and chelating agents added), have been formulated to replace acid cleaners. The most common method for using aqueous cleaners is the soak tank or soak cleaning method. Since the equipment used is almost identical to the equipment used for solvent soak cleaning, the reader is referred to the previous paragraph on soak cleaning. The only additional method that deserves special discussion is the electrochemical cleaning method.

Electrochemical cleaning is similar to an electroplating operation in that the work piece is connected to a source of current. Cleaning is achieved by the scrubbing action of the gases generated at the electrodes. With direct current cleaning, the metal part is attached to the cathode. Hydrogen gas is liberated at the part's surface and provides the scrubbing action. Since the volume of hydrogen released at the cathode is greater than the volume of oxygen released at the anode, scrubbing action is greatest at the cathode. Offsetting this advantage is the potential for smut formation (metal contaminants in the solution plate onto the part) and the possibility of hydrogen embrittlement of the metal. With reverse current cleaning, the part is attached to the anode. While the cleaning effectiveness is less than with direct current cleaning, smut formation and hydrogen embrittlement are prevented. The only major disadvantage of reverse current cleaning is that many metals are subject to attack (some of the metal will dissolve into the solution and plate onto the cathode). Electrochemical cleaning is often employed prior to electroplating and after vapor degreasing, soak cleaning, and/or acid cleaning.

Water, the final cleaning medium, is usually used in a soak tank and/or spray unit. The importance of water as a cleaning medium is that almost every cleaning operation mentioned requires that a primary water wash be performed before and after each operation. By preventing cross contamination of various cleaning media (for example, the dragout or carryover of alkaline solution into an acid bath), the life of a solution is extended and the overall cleaning efficiency is maintained. Since proper cleaning requires an exacting sequence of operations, water use is an integral part of any cleaning operation.

7. WASTE DESCRIPTION

The primary specific wastes associated with metal parts cleaning are listed in Table 7-1, along with their sources. Generally, these wastes are produced whenever the level of contamination in the cleaning media inhibits efficient cleaning. The composition of the waste will depend on the cleaning media used and the type of soil removed (oils, greases, waxes, metallic particles, oxides, etc.). The types of waste produced are largely independent of the nature of the plant.

If a facility has a wastewater treatment system, alkaline and acid cleaning solutions, along with primary rinse water waste are mixed together (one acts to neutralize the other) and then treated. Secondary rinse water (if a secondary rinse is used) is usually used to replace discarded primary rinse water or used as a makeup for cleaning solutions. For facilities using small amounts of cleaner, the tendency is to drum the material for disposal. Solvent waste is normally drummed for disposal or sold to an off-site recycler. The only on-site recycling being performed is by companies using vapor degreasers.

8. WASTE GENERATION RATES

Metal parts cleaning operations generate waste comprised of abrasives, solvents, aqueous cleaning solutions, and spent rinse water. Except for the solvent waste, all of the waste streams are very much diluted with water. Aqueous cleaners are usually sold at various levels of concentration that must then be diluted before use. Based on a review of available literature and information from industry contacts, a profile of the wastes generated from metal parts cleaning operations in the U.S. was estimated by project staff and is shown in Table 9-1. This profile shows a fractional share of each waste stream in the total stream generated based on weight.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

The list of individual primary waste streams and their sources along with a list of source reduction methods is presented in Table 9-1. The following sections discuss recommended waste reduction methods and identified procedures. The basis for identification of those methods came from published accounts in the open literature.

Table 7-1 Metal Parts Cleaning Wastes

No.	Waste Description	Process Origin	Composition	RCRA Code
1.	Abrasives	Removal of rust; scale polishing of metal	Aluminum oxide, silica metal, water, grease	-
2.	Solvents	Removal of oil-based soils	Halogenated and non-halogenated solvents, oil-based contaminants	F001 F002 F003 F005
3.	Alkalines	Removal of organic soils, descaling	Alkaline salts, additives, organic soils, water	F009
4.	Acids	Removal of scale, smut	Acids, additives, oxides, metal, water	-
5.	Rinse water	Removal of previous cleaning material	Water with traces of cleaners and additives	-

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" have also been included. Good operating practices are defined as procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practice:

- o Waste stream segregation
- o Personnel practices
  - Management initiatives
  - Employee training
- o Procedural measures
  - Documentation
  - Material handling and storage
  - Material tracking and inventory control
  - Scheduling

- o Loss prevention practices
  - Spill prevention
  - Preventive maintenance
  - Emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Abrasives

Abrasive powders are usually mixed with an oil-based or water-based binder and are then applied to a polishing or buffing wheel. Waste from this operation consists of worn out cloth wheels saturated with abrasive, metal particles, binder, and various oxides. Wastes from vibratory or mass finishing operations consist of abrasive, metal particles, water, and oxides dispersed in a slurry. Alkaline or acid cleaners are sometimes added to the slurry so that additional cleaning action is provided. Usually, slurries are discarded when the abrasive has undergone a given amount of attrition or breakdown. The following source reduction methods were noted for abrasive cleaners:

- Use of greaseless or water-based binders for polishing or buffing.
  When oil-based binders are used, the frictional heat generated during buffing can cause the binders to burn. This, in turn, leads to the requirement for additional cleaning e.g. using alkaline soaking. When properly used, greaseless compounds produce an object that leaves the wheel clean and dry (Durney 1984, Chap. 3B). Also, greaseless compositions tend to adhere to the surface of the wheel so that wheel life is extended.

- Use of liquid spray compositions.
  Most abrasive compositions are formulated for use in bar form (the bar is held against the wheel to apply abrasive). With a liquid spray system, a spray gun applies the compound to the wheel automatically. Since the optimum quantity of compound is always maintained on the wheel, wheel wear due to compound deficiency, compound waste due to over-application, and the requirement for subsequent cleaning (spray compounds are usually water-based), are all significantly reduced or eliminated (Durney 1984, Chap. 3B).

- Careful control of water level in mass finishing equipment.
  If not enough water is used, work items leaving the equipment will be dirty. In addition, too little water will increase the attrition rate of the abrasive and increase replacement frequency (Durney 1984, Chap. 3C).

9.1.2 Solvent Cleaners

Solvents are used for various cleaning operations by a large segment of industry. By far, the most common equipment item used is the soak tank, followed by the vapor degreaser. While much more attention has been focused on vapor degreaser operation because of its much greater potential for producing air pollutants, it should not be overlooked that the main methods for reducing waste from both equipment items are the same. Basically, the two most important source reduction goals are to minimize solvent vapor loss and to maintain solvent quality. By reducing solvent vapor loss, the composition of the solvent remains as close as possible to the solvent's original composition. Solvents contain chemical stabilizers that help prevent acid formation

and remove acid contaminants from the bulk of solution. As solvent is used, its ability to neutralize or prevent acid formation lessens. Unless measures are taken to prevent a solvent from going acid, the entire quantity of solvent has to be replaced periodically. By maintaining the solvent's quality, the need for replacement is reduced. The following source reduction measures were considered as ways of reducing waste due to solvent cleaning operations (methods for reducing waste due to solution drag-out are discussed in Section 9.1.5, Rinse Water):

- Installation of lids on tanks.
  Lids should be placed on all tanks when they are not in use. By using a cover during periods of non-use, vapor degreaser solvent loss can be reduced by 24 to 50 percent. Additional reductions have been achieved by using covers designed to allow for use even while the cleaning operation is in progress (Durney 1984, Chap. 3E). Known as "silhouette entries", they are covers with opening shapes that match the shapes of the parts being degreased and therefore minimize the area for vapor loss*. Solid covers should be designed to slide closed horizontally across the open surface. This disturbs the vapor zone less than covers that are hinged.

- Increase in freeboard space.
  Freeboard is the distance between the top of the vapor zone and the top of the tank. Early vapor degreaser designs called for a freeboard equal to 50 percent of the tank's width. In the mid-1970's, EPA regulations recommended a freeboard of 75 percent. This reduced emissions by 27 to 46 percent, based on experimentation. For shops where air turbulence is present, increasing the freeboard to 100 percent can provide an additional 39 percent reduction (Durney 1984, Chap. 3E). As was previously stated for installing lids, increasing the freeboard on all soak tanks should be equally effective.

- Installation of freeboard chillers in addition to cooling jackets.
  With this approach, a second set of refrigerated coils is installed above the vapor degreaser's condenser coils. These coils chill the air above the vapor zone and create a secondary barrier to vapor loss. Reductions in solvent

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* Westinghouse Electric Corp. 1985: Personal communication.

consumption of up to 60 percent have been measured in practice. Unfortunately, water contamination of the solvent can occur due to frost build-up on the coils. Therefore, special water collection equipment is also required. For systems using azeotropic co-solvents that are water soluble (such as alcohols), the potential for water contamination makes this method impractical (Durney 1984, Chap. 3E).

- Better operating practices.

  Cross-contamination of solvent is a common occurence, especially when the types of solvent being used have similar sounding names. As little as one-tenth of one percent 1,1,1-trichloroethane mixed into a tank of trichloroethylene can cause an acid condition (Smith 1981).

  Just like solvent cross-contamination, water contamination can lead to acid formation. In addition, water contamination can form minimum boiling azeotropes (a mixture of solvent and water, inseparable through simple distillation, with a lower boiling point than water or solvent alone). To avoid water contamination, the water separator should be cleaned and checked frequently for proper drainage. Next, the temperature of the water exiting the condenser coils should be maintained at 90 to 100°F. If the temperature is too low, moisture will condense out of the air. Finally, parts should be checked to see that they do not enter the degreaser while wet. This may call for using oil-based abrasives and cutting oils in production steps prior to cleaning (Smith 1981).

  Sludge that collects in the bottom of the tank should always be removed promptly. Contaminants, such as paint, absorb solvent, dissolve into solution, and reduce cleaning efficiency (Durney 1982). Zinc and aluminum fines, which are particularly reactive in chlorinated solvent, can lead to acid formation if allowed to collect. Organic soil contamination should not be allowed to exceed 10 percent for cold cleaning operations and 25 percent for vapor degreasers. When these levels are exceeded, acid formation can occur. While most solvents used in vapor degreasers are cleaned by distillation and reused, waste solvent from cold cleaning operations is normally drummed and disposed of (Payne 1961).

As solvents are used, their ability to neutralize acid lessens. Normally, when an acid acceptance test indicates that a solvent is close to going acid, fresh solvent will be added to boost the level of stabilizers in the tank. This, however, is a poor solution, since the level of stabilizers in the tank can never be made equal to the level of stabilizers in fresh solvent. The proper solution is to analyze the solvent and add specific components rather than fresh solvent. Usually, the expense of analysis will be offset by the savings in solvent for tanks of 500 gallons or more (Durney 1982). This method should also be useful for facilities that recycle their solvent, since distillation usually removes most stabilizers from the solvent.

For facilities using a large number of cold cleaning tanks, standardizing the solvent used would help by making the potential for recycling more attractive. Standardizing, in this context, means using a minimum (preferably one) type of solvent in all operations in the plant. Many times, the decision to use a certain type of solvent as opposed to another is based on an operator's preference, rather than a technical need or requirement. In addition, the amount of waste generated from a single cold cleaning tank is small, so that the potential for recycling is seldom considered.

Once standardization has been implemented, the next step would be for companies to consider the possibility of consolidating cold cleaning operations into a centralized vapor degreasing operation. While cold cleaning solvents must usually be discarded when the level of contamination exceeds 10 percent, vapor degreasers can operate up to a level of 25 to 30 percent. In addition, vapor degreasers provide a much better level of cleaning and the parts leave the unit dry. Another advantage of consolidation would be that all solvent handling would occur at a centralized location.

Other waste reduction techniques based on better operating practices would be to locate cold cleaning tanks away from heat sources, control the amount of heat supplied to vapor degreasers, avoid spraying parts above the vapor zone or cooling jacket, and avoid solvent vapor drag-out.

Solvent vapor drag-out, or solvent vapor removal from the tank, occurs when a work piece is inserted or withdrawn from the tank too quickly. The speed of the work should not exceed 11 feet per minute. In addition, the geometry of the work piece can affect drag-out. If the space between the wall of the tank and the work piece is too narrow, then a piston effect will occur and solvent vapor will be forced out of the tank. As a general measure, the cross-sectional area of the work load should not exceed 50 percent of the tank's open area (Smith 1981). Drag-out of the solution or solvent is further discussed in Section 9.1.5.

9.1.3 Alkaline Cleaners

Alkaline cleaners are used to remove a wide variety of organic contaminants from metal surfaces. The most common equipment used is a heated soak tank with spray unit. Alkaline cleaners are viewed as viable substitutes for solvents. The following source reduction methods for reducing wastes due to the use of alkaline cleaners (except for solution drag-out) were noted:

- Remove sludge frequently.

  Waterloo Industries, Inc. in Waterloo, Iowa manufactures steel cabinets that are alkaline cleaned prior to phosphate coating. Waterloo installed a 100 gallon per minute Liquid-Life separator unit designed to remove sludge and particulate matter continuously from the alkaline bath. The unit consists of a pump, hydrocyclone, and sludge retention tank. Since the unit was installed, replacement chemical costs have been reduced 20 percent, the time interval between dumping and total cleanout of the system has been lengthened from four to thirteen weeks, and maintenance associated with the cleaning process has been reduced because a pump is the only moving part in the system. Liquid-Life claims that the system can also be used for solvent and acid cleaning operations (Anonymous 1982).

- Better operating practices.

  All parts that enter the soak tank should be free of solvent or acid. The best way to ensure this is to practice efficient rinsing of the part. For parts that are first mechanically cleaned, water-based abrasives and cutting oils should be used. This reduces the cleaning load (i.e., oil) that enters the cleaning tank and hence extends solution life.

9.1.4 Acid Cleaners

Acid cleaners are used to remove oxidation, scale, and rust from metal surfaces. The most common equipment used is a heated and lined soak tank. Since the basic equipment and operating procedures used with acid cleaners are very similar to alkaline cleaners, the source reduction methods are the same.

9.1.5 Rinse Water

Water is used to remove or dilute cleaning solutions that are dragged out with cleaned parts. If these cleaning solutions are not removed, they can affect the quality of the work and contaminate subsequent cleaning and processing operations. Since rinsing is essentially a process of dilution, the general trend in the past was to use large volumes of water. Today, however, efficient rinsing is required to achieve the proper level or degree of dilution and conserve water. By conserving water, capital and operating costs for waste treatment unit are minimized. Source reduction methods considered for reducing the amount of cleaning solution drag-out and reducing the amount of water required are:

- Proper design and operation of rack system.

  Through proper design and operation of a rack system, solution drag-out can be significantly reduced. Parts should be racked so that the surface is nearly vertical and the longest dimension is horizontal. Also, the lower edge should be tilted from the horizontal (this allows run-off to occur at a corner rather than the entire edge). Withdrawal from the cleaning solution should be made slowly and the part allowed to drain over the tank for a minute or two. Additional drainage time can be provided by installing sloped drain boards at the end of the tank. As shown below, proper racking can reduce solution drag-out (Durney 1984, Chap. 32).

Item	Drag out gal/1000 ft^2
Vertical parts, well drained	0.4
Vertical parts, poorly drained	2.0
Vertical parts, very poorly drained	4.0
Horizontal parts, well drained	0.8
Horizontal parts, very poorly drained	10.0
Cup-shaped parts, very poorly drained	8.0 to 24.0+

For items with cup-shaped recesses, drainage can be a difficult problem. If the part cannot be positioned to allow for drainage, special measures must be taken. Some of these measures include drilling or repositioning drain holes in the part, tilting the rack as its removed from the bath, and/or installing air-jets to blow off cleaner solution from the part.

As a final point, rack maintenance should not be overlooked. If rack insulation is cracked, solution can be carried out in the gaps and fissures. In addition, exposure of the rack metal during electroplating operations can lead to contaminated bath solutions. Uninsulated racks used for cleaning should be stripped regularly since the rough surface will hold solution by capillary action. Rack maintenance should be viewed as a routine operation and not something to perform when a problem develops.

- Proper design and operation of barrel system.
  While barrels are normally fully immersed during electroplating operations, maximum rinsing efficiency occurs when the barrel is only immersed partially. The proper depth and rate of rotation depends on many factors but normally occurs when the barrel is immersed to about 38 percent of its diameter. In most plants, rinse tanks for barrel operations are designed and operated the same way as electroplating baths (i.e., the barrel is fully immersed). After immersing the barrel, it is raised over the tank while rotating and allowed to drain. This operation should always be performed twice over each rinse tank. Normally, however, the barrel is only rinsed once or is not drained properly. In addition, many facilities employ only one rinse tank. At a minimum, two counterflow cold rinses and a final hot rinse should always be used (Durney 1984, Chap. 32).

- Proper installation and operation of rinse tanks.
  Since the process of rinsing is one of dilution, good practice should assure that the rinse tank is well mixed at all times. Tanks can be mixed by agitating the water with oil-free air, introducing fresh water at the bottom of the tank, and by other mechanical means. The water in the tank should exhibit a rolling turbulence without undue splashing. For cleaners that are not very easy to rinse off, heated rinse tanks are often employed.

Once agitation and complete mixing in the tank have been assured, the next concern is the sequencing of rinses. Pinkerton and Graham (Durney 1984, Chap. 32) presented the mathematical derivation of rinsing equations proposed by several authors for five different rinsing systems. For each case, the drag-in and drag-out volumes and concentrations were held constant. The five systems examined, along with the flow rates required to maintain equilibrium, are listed below.

System	Flow gpm
1. Single rinse	10.0
2. Two rinses in series, equal flows of fresh rinse water to each tank.	0.6
3. Three rinses in series, same condition as in 2.	0.3
4. Two counterflow rinses, fresh water feed to second tank only.	0.3
5. Three counterflow rinses, fresh water feed to third tank only.	0.1

Based on these results, the conversion from a single rinse to a counterflow rinse system can be well justified. For facilities with limited floor space, single rinse tanks can often be converted by welding one or more dams across the tank. For manual operations, the dams are designed to rely on an overflow or cascade action, while automated systems would require pumps to be installed. Most modern facilities are designed with multiple rinse tanks after each cleaning operation. While theoretical wastewater reductions of 90 percent have been reported (USEPA 1983), the actual reduction expected would be closer to 66 percent*.

- Installation of water sprays on rinse tanks.

  For installations with single rinse tanks and limited space, rinsing efficiency can easily be increased by installing a spray system. By spraying work items with fresh water as they are raised above the rinse, the equivalent of an extra one-half counterflow bath is obtained (Durney 1984, Chap. 32). Sprays should be properly designed to provide uniform coverage or rinsing of the part and not produce undue splashing. Spray rinsing is also beneficial on multitank counterflow systems where each spray unit is fed water from the succeeding rinse tank.

* National Association of Metal Finishers 1985: Personal communication.

- Installation of fog nozzles on heated aqueous cleaner tanks.

  A fog nozzle is a special high pressure water spray unit that produces a finely atomized mist of water or fog. Since the water is so finely dispersed, only a small amount of water is used compared to a normal spray unit. Therefore, fog nozzles can be used over heated cleaner tanks for rinsing work items without introducing a surplus of water. Two main benefits of using fog nozzles are that they help cool the part so that the cleaning solution has less chance of drying on the part and that they reduce drag-out by diluting the solution retained on the part. The elimination of rejects and the reduction of drag-out from cleaner and plating baths through the use of fog nozzles has been reported (Durney 1984, Chap. 32).

- Chemical rinsing.

  In some facilities, rinse water from an alkaline cleaning operation is reused to rinse parts from an acid cleaning operation*. The basic premise is to combine rinsing and waste treatment in one operation. While this procedure would reduce the amount of waste rinse water generated and reduce the degree of waste water treatment required, the potential for contaminating the parts with metal hydroxide precipitates would be increased. Therefore, this method would be limited to those parts not requiring rigorous cleaning.

- Use of deionized water for rinsing.

  Use of regular tap water is a major source of impurities in any closed loop system. By using deionized water, many rinses can be reclaimed using a simple evaporation system. In addition, use of deionized water can extend plating bath life by reducing impurity drag-in and reduce the number of rejects produced. Many packaged systems commercially available can supply deionized water of adequate quality (most electroplaters do not require extremely high purity water). (Durney 1984, Chap. 5).

9.2 Implementation Profile

The principal source control methods discussed for reducing waste from metal cleaning operations are proper equipment operation, maintenance of cleaning solution integrity,

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* National Association of Metal Finishers 1985: Personal communication.

and installation of counterflow rinse tanks with spray or fog nozzles. These measures are technically simple. A major constraint, however, on the implementation of counterflow rinsing is in its large space requirement. Many older facilities would have difficulty in finding the space needed for extra tanks.

As increased regulation raises the cost of waste disposal and treatment, efforts to decrease waste volumes become economically justifiable. Spending to reduce cleaning waste can produce treatment and disposal cost savings which more than offset the expenditure. In addition, material costs can be cut since the life of the cleaning solutions will be lengthened. Aside from the expense of having to make space for extra equipment in some facilities, most of the measures discussed in this study would involve minimal capital outlays (e.g., proper equipment operation requires only that management thoroughly train the employees using the equipment and that the equipment be correctly maintained). These low-cost measures generally have a fast payback and are among the first a firm should implement. Furthermore, an increased awareness on the part of production process designers that waste generation due to cleaning operations is a significant (yet variable) operating cost, can result in a substantial cost avoidance once production is underway.

9.3 Summary

Table 9-1 presents summary data on metal parts cleaning waste sources and control methods. The rankings shown in the table were based on review of the available literature. It is estimated that reductions in waste generation that have occurred as a result of practicing the noted methods are significant, as evidenced by a current reduction index of 2.0 (50 percent). By implementing additional waste reduction measures or increasing the use of existing measures, the amount of waste currently being generated can be reduced significantly, to a level characterized by a future reduction index of 1.2 to 1.9 (30 to 48 percent). The most effective measures for achieving this reduction include better operating practices, and frequent removal of sludge from alkaline and acid cleaners.

10. WASTE REDUCTION THROUGH MEDIA SUBSTITUTION

Since the choice of which cleaning medium to use is seldom clear cut, many opportunities exist for substituting one cleaning medium with another. Currently,

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR METAL PARTS CLEANING

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Abrasives	1. Use water-based binders	1	2	1	2	2		0.5	0.3	
	2. Use liquid spray compositions	1	2	2	1	2		0.5	0.8	0 8
	3. Control water level in equipment	1	2	2	3	3		1.5	0.4	
	Overall	1.00	2 00	1 67	2.00	2 33	0.00	1.5	0.5	0.8
Solvent Cleaners (*)	1. Install lids/silhouettes on tanks	3	2	2	2	2		1.0	0.5	
	2. Increase freeboard space on tank	2	2	2	2	2		1.0	0.5	
	3. Install freeboard chillers on tanks	2	2	3	1	2		0.8	1.1	
	4. Implement better operating practices	3	2	4	2	4		2.0	2.0	2 0
	Overall	2 50	2.00	2.75	1.75	2.50	0.04	2.0	1.0	2.0
Alkaline Cleaners (*)	1. Remove sludge frequently/continuously	2	3	3	1	3		0.8	1.7	1.7
	2. Install lids on tanks	0	0	1	1	3		0.3	0.6	
	3. Implement better operating practices	2	2	3	2	4		1.5	1.5	
	Overall	1.33	1.67	2 33	1.33	3.33	0.33	1.5	1.3	1 7
Acid Cleaners	1. Remove sludge frequently/continuously	2	3	3	1	3		0.8	1.7	1 7
	2. Install lids on tanks	0	0	1	1	3		0.3	0.6	
	3. Implement better operating practices	2	2	3	2	4		1.5	1.5	
	Overall	1 33	1.67	2.33	1.33	3 33	0.12	1.5	1.3	1.7
Rinse Water	1. Operate rack system properly	3	3	3	3	4		2.3	0.8	
	2 Operate barrel system properly	1	3	4	2	4		2.0	2.0	2 0
	3 Operate rinse tanks properly	2	3	3	2	3		1.5	1.1	
	4 Install water sprays on rinse tanks	2	3	3	2	3		1.5	1.1	
	5 Install fog nozzles on heated tanks	1	3	3	2	3		1.5	1.1	
	6 Use chemical rinsing	1	1	2	1	1		0.5	0.4	
	7. Use deionized water for rinsing	1	2	2	1	3		0.5	1.1	
	Overall	1.57	2.57	2 86	1 86	3 00	0 51	2.3	1 1	2 0
All Sources	All Methods						1.00	2.0	1 2	1 9

(*) These waste streams include listed "F" and/or "K" RCRA wastes.

there is a major effort to switch from cold tanks using non-halogenated solvents and vapor degreasers using halogenated solvents to cold tank alkaline and emulsion cleaners. This major change-over is, in large part, caused by the regulatory pressure to reduce air emissions from degreasing operations.

Detailed cost estimates comparing vapor degreasing and cold cleaning operations with abrasives, alkaline cleaning, and emulsion cleaning systems were presented in a recent report (GCA 1983). For all substitutions except abrasives, solvent cleaning had lower operating costs than either alkaline or emulsion systems. Major disadvantages of cleaning media substitutions were that use of abrasives was limited to parts with simple shapes, use of alkaline cleaners did not always leave the parts as water-free as required, and use of emulsion cleaners left an oil film on the part that required additional cleaning. Since no information was provided concerning the effect of substitution on waste generation rates, no recommendations can be made except for the substitution of solvent and/or alkaline cleaning solutions with abrasives. Extensive application of this method can be made by facilities engaged in paint stripping from metal parts which is covered in the study of paint application.

While stricter environmental air pollution laws are forcing a shift away from solvent degreasing operations towards greater use of alkaline or emulsion cleaners, client specifications often force many job shops to perform certain operations in a specific way. Whereas captive shops can usually perform any type of cleaning so long as a certain level of cleanliness is maintained, job shops must clean parts according to the standards and methods specified by the client. Many of the standards dictate not only the type and cleaning sequence to be employed, but also the number of rinse stages to be used between each step. Therefore, the revision of standards can be an effective way of minimizing waste.

11. CONCLUSIONS

While industries engaged in metal parts cleaning operations have done much to reduce the amount of waste they generate, it appears that further reductions are possible. Our estimates indicate that possible waste reductions range from 30 to 48 percent. Several methods that appear promising for the industry as a whole would be to implement better operating practices on all systems, and frequently remove the sludge from aqueous cleaners. Especially in light of rising disposal costs, many of the

proposed waste reduction measures are cost effective, and are justifiable on economic as well as environmental grounds.

In general, it could be useful if the organizations that set cleaning criteria or standards review them in the context of associated waste generation.

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13. INDUSTRY CONTACTS

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David Anzures, National Association of Metal Finishers, San Fernando, CA.

Walter G. Vaux, Process and Chemical Engineering, Westinghouse Electric Corp., Pittsburgh, PA.

1. PROCESS: PAINT APPLICATION

2. SIC CODE: XXXX

3. INDUSTRY DESCRIPTION

The application of paint is practiced in most industries, and thus does not have an individual Standard Industrial Classification (SIC) code. Usually, industries engaged in paint application can be segregated according to one of three paint or surface coating classifications: architectural, product, or special purpose. Industries using architectural paints would be engaged in construction activities; (this would include building contractors, painters, and home repairers). Product coatings would be used by industries engaged in manufacturing durable goods, such as automobiles, appliances, furniture, etc. The last classification, special purpose coatings, would include organizations involved in industrial, military, and highway maintenance. Also included would be any person or industry using aerosol spray paints.

4. PRODUCTS AND THEIR USES

Due to the diversity of the industries utilizing paint application as part of their operation, a comprehensive listing of all the products that are painted would be beyond the scope of this report. Basically, surface coatings are used wherever it is desired to provide decoration, protection, and/or safety marking to a product or item.

5. RAW MATERIALS

In 1983, the paint manufacturing industry sold $8.6 billion worth of paint. This represented 463 million gallons of architectural coatings, 331 million gallons of product coatings, and 130 million gallons of special purpose coatings (Webber 1984). While most of the architectural coatings sold were water-based, most product and special purpose coatings were solvent-based. For additional details concerning the types of paint and the industries that utilize them, the reader is referred elsewhere in this appendix to the process study on paint manufacturing.

6. PROCESS DESCRIPTION

Detailed process descriptions regarding paint application can be found in the open literature (Payne 1961, Letsky 1960, Campbell and Glenn 1982). The following discussion highlights the various types of equipment used for applying product coatings and the supporting operations required for producing a finished product.

Before a product coating can be applied to a surface, the surface must be free from contamination. Many different types of abrasives, alkalines, acids, and solvents are used by industry to clean metal surfaces. Because of the complexity and diversity of the contaminants, many different cleaning operations are usually required. In addition, extensive use of water is required to rinse the parts free of cleaning solution so that residual cleaner does not contribute to the contamination problem. Once a part is cleaned, surface treatment such as phosphate coating can be applied if desired. The purpose of surface treatment is to condition or prepare the surface so that the paint forms a better bond with the metal surface. For detailed physical descriptions characterizing cleaning and metal surface treatment operations, the reader is referred to those studies in this appendix.

After the item has been cleaned and treated, paint can be applied. Depending on the size, shape, complexity, and quantity of items to be painted, different application methods can be employed. When it is desired to paint a large number of very small items, the most commonly used methods are tumbling, barreling, or centrifuging. For all three methods, the parts are placed inside a barrel, solvent-based paint is poured onto the items, and the barrel is then rotated. After a short time and at the correct point of tackiness, the parts are transferred to an oven in a wire basket. If the time in the barrel is too short, the parts leaving the oven will be stuck together. If the time in the barrel is too long, the finish will be damaged and marred. While paint consumption using these methods is very small, the empirical nature of the operation requires that the operator be highly experienced to achieve reliable results.

For cylindrical items, a commonly used method is dipping. Here the paint is held in a large tank and the object to be painted is slowly lowered into the tank and then withdrawn. Many complex items can be dip painted provided that the drainage points, (the places where the excess paint drips off), can be located where they are not

noticeable. Items as large as refrigerators, washing machines, and automobiles have been dip painted. A variation of dip coating or dipping is electrocoating. A water-based paint is mixed into a large tank of water and given an electrical charge. The object to be coated is connected to an electrical ground and the electrostatic potential causes the paint particles to plate onto the object's surface. As the thickness of paint builds up, most of the water is forced out of the paint so that the coating adheres tightly to the surface. Following coating operation, water sprays are used to rinse the object, with the rinse water being returned to the main dip tank.

Flow coating is often employed for items that would be difficult to dip because of their size or shape, or as a means of avoiding the installation and operation of large dip tanks. A flow coating system operates by using high pressure sprays to flood the item with solvent-based paint. After spraying, the item is allowed to drain and the excess paint is recirculated. Since a considerable amount of bubbling occurs due to spraying, the item is then passed through a solvent chamber where the solvent vapors allow the paint to reflow. Following this operation, the item is then oven-dried. The main disadvantage of flow coating is high solvent loss, which can be three times as large as for dipping and twice as great as for spraying.

For relatively flat items of large area, roller coating and curtain coating machines are used. Roller coating is used extensively by the canning industry for painting flat metal sheets that are then fabricated into cans. It is also used for spreading or applying glue to wood in the manufacturing of plywood. A roller coating machine operates by metering paint or coating material onto a roller and then transporting the item past the roller by means of a conveyor belt. Curtain coating machines were originally used for coating candies with chocolate and are presently being used in the furniture industry (for table tops, doors, etc.) and the electronic manufacturing industry. A curtain coating machine consists of a long, horizontal rectangular pressurized container that is placed at a right angle to the direction of work flow. Along the bottom of this container is an adjustable slit that allows the coating to flow and form a vertical curtain. A conveyor belt is placed on each side of the curtain so that work items are passed through the curtain and coated without the conveyor belts being coated. When items are not being coated, the paint flows between the two conveyors, is collected in a trough, and then pumped back up to the curtain head. Coating thickness can be controlled by the speed of the conveyor belt.

While all of the above-mentioned methods have found widespread acceptance by industry, the most widely used method for applying paint is still the spray gun. A spray gun operates by using compressed air, to atomize the paint and produce a fan or circular cone spray pattern. Many installations are automated so that a fixed gun is turned on when an object passes in front of it. In its simplest use, the gun is hand-held and the object remains stationary. Some of the variations on spray gun painting are airless spray guns and electrostatic spray guns. Airless spray guns force the paint out at high pressure so that air is not required for atomization. By eliminating the use of compressed air, operating costs are lower, spray mists are not produced, and expensive exhaust systems are not required. Electrostatic spray units are designed so that the atomized paint leaving the gun has a positive charge. This positive charge causes the paint to be attracted to the object which is connected to ground. Since more of the paint reaches its target (thereby reducing overspray), less waste is generated. Other spray systems, besides hand-held guns, include revolving bells and discs that rely on electrostatic and centrifugal forces to atomize the paint. Since neither of these last two methods relies on air, their advantages are similar to those for the airless spray gun.

Following the application of paint, the item is passed through a drying or curing oven. The curing methods employed, infrared or ultraviolet, will depend on the type of paints being used. Once dried, the items are sent to inspection and final packaging or assembly. If a part fails inspection because of a bad finish, it is usually reworked by stripping off the paint and returning it to the cleaning operation. A block flow diagram of the operation used in product coating application is presented in Figure 6-1.

7. WASTE DESCRIPTION

The primary specific wastes associated with product coating application are listed in Table 7-1, along with their primary sources. Waste would consist of empty paint containers, spent cleaning solutions, paint overspray (including paint collected by air pollution control equipment), spent stripping solutions, and equipment cleaning wastes.

8. WASTE GENERATION RATES

Paint application operations generate waste comprised of empty containers, solvents, aqueous (alkaline and/or acidic) cleaning solutions, rinse water, paint stripper, and

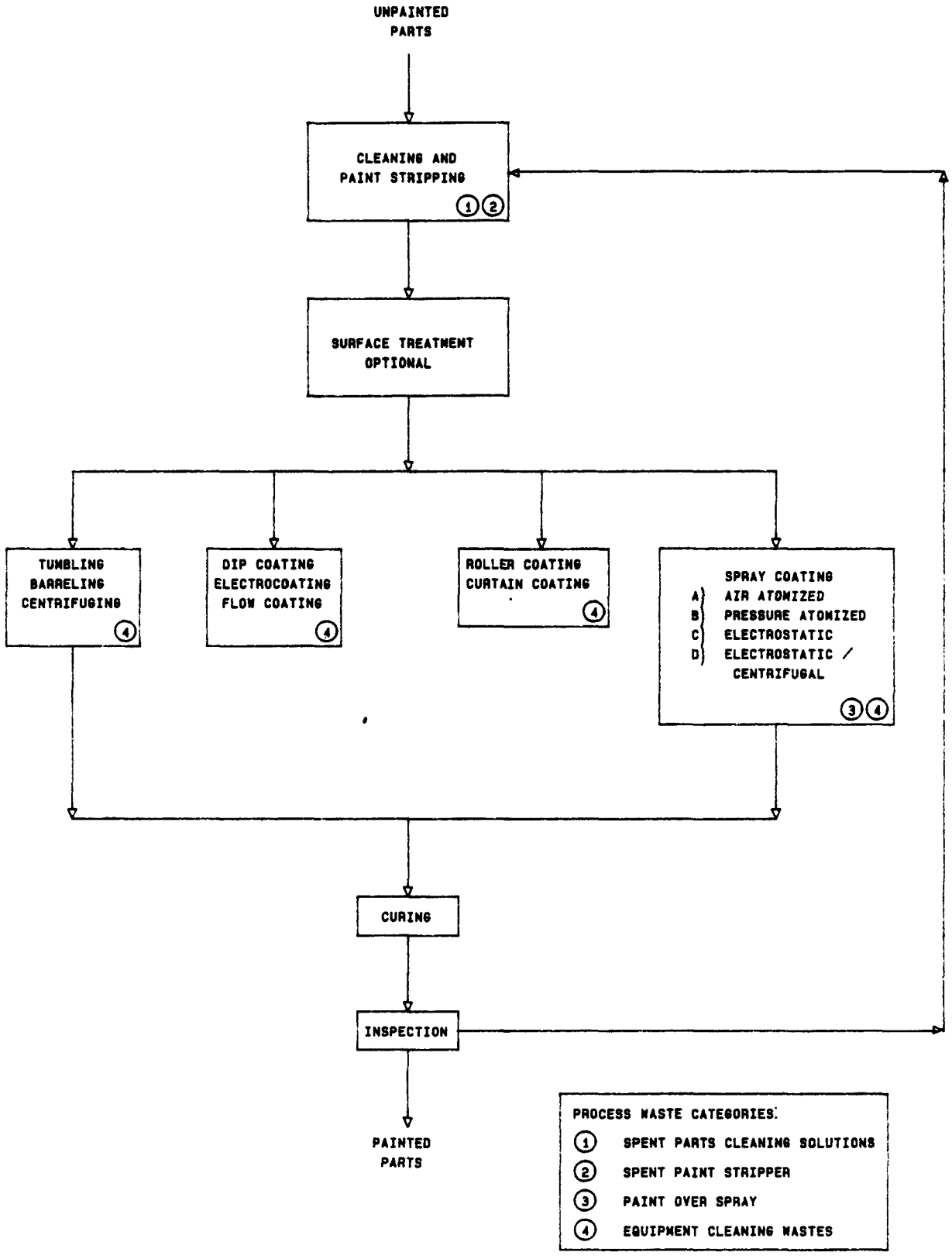

Figure 6-1 Paint Application

Table 7-1 Paint Application Wastes

No.	Waste Description	Process Origin	Composition	RCRA Codes
1.	Leftover paint in metal gallon cans	Raw materials	Metal can with a few ounces of paint inside	-
2.	Spent solvent	Cold cleaning and/or vapor degreasing	Halogenated and non-halogenated solvents, oil-based contaminants	F001 F002 F003 F005
3.	Spent alkaline cleaners	Removal of organic soils, descaling	Alkaline salts, additives, organic soils, water	-
4.	Spent acid cleaners	Removal of scale, smut	Acids, additives, oxides, metal, water	-
5.	Rinse water	Removal of previous cleaning solutions	Water with traces of cleaner	-
6.	Paint	Overspray from paint application	Paint	-
7.	Paint stripper	Stripping of bad paint from parts	Non-halogenated solvents, paint	F003
8.	Water and/or solvent	Cleaning of equipment	Halogenated and non-halogenated solvent, water, and paint	F002 F003 F005

equipment cleaning wastes. A survey of the available literature did not yield waste generation rates for these various waste streams. In addition, volume estimates would be difficult, due to the diverse types of operations being performed throughout the industry. Therefore, only fractional waste generation data (the percentage of waste each stream represents as compared to the total waste generated), could be estimated by project staff, based on the available information and industry comments. These values are shown in Table 9-1.

9. WASTE REDUCTION THROUGH SOURCE CONTROL

9.1 Description of Techniques

The list of individual primary waste streams and their sources, along with a list of source reduction methods, is presented in Table 9-1. The following sections discuss recommended waste reduction methods and identified procedures. The basis for identification of these methods came from published accounts in the open literature.

In addition to the waste reduction measures classified as being process changes or material/product substitutions, a variety of waste reducing measures labeled as "good operating practices" have also been included. Good operating practices are defined as procedural or institutional policies which result in a reduction of waste. The following items highlight the scope of good operating practices:

- o Waste stream segregation
- o Personnel practices
  - Management initiatives
  - Employee training
- o Procedural measures
  - Documentation
  - Material handling and storage
  - Material tracking and inventory control
  - Scheduling
- o Loss prevention practices
  - Spill prevention
  - Preventive maintenance
  - Emergency preparedness

For each waste stream, good operating practice applies whether it is listed or not. Separate listings have been provided whenever case studies were identified.

9.1.1 Empty Containers

Facilities that use small quantities of paint and a large variety of color often purchase paint in small cans and containers (less than five gallons) for use in spray gun equipment. After emptying the can of paint into the spray gun's holding cup, a coating of paint remains inside the can. Since these cans are seldom cleaned, the entire can must be discarded as waste. Also included in this waste stream would be outdated or leftover paint removed from storage. The waste reduction methods are as follows:

- Better operating practices.
  By preventing the contamination of non-hazardous materials such as trash, with potentially hazardous materials such as solvent-based paint, the volume of hazardous waste is minimized. Good examples of hazardous and non-hazardous waste segregation were identified in the paint manufacturing process study.

  Container waste is generated by the paint that remains inside a can after the can is emptied and by the paint that is placed in storage, not used, and becomes outdated. Facilities should strive to consolidate paint use so that the purchase of paint in bulk is practical. Since one large bulk container has much less surface area than an equivalent volume of small cans, the amount of wasted paint is much less. Large bulk containers can often be returned to the paint manufacturer for cleaning and reuse; (while cleaning still generates some waste, the paint manufacturer is in a better position to handle it).

  When the purchase of paint in bulk containers is not practical, then paint should be purchased in the smallest amount required so as to minimize the amount of residual. Workers should not open a one gallon can of paint when only a quart or two are required. It should be assumed that any paint that is left over will require disposal as a waste. While the per unit cost of paint when purchased in various small quantity containers is greater than the cost of paint when purchased in larger quantities, the savings in reduced paint wastage and disposal costs could still be substantial.

9.1.2 Parts Cleaning Waste

Wastes associated with parts cleaning would consist of spent solvent, alkaline and/or acid baths, rinse water, and whatever contaminants were removed. Since the methods used to minimize waste from the cleaning operation are highly specific to the types of cleaning methods employed and because the subject of cleaning is so diverse, it is recommended that the reader refers to the study elsewhere in this appendix on metal parts cleaning for additional information. Note that paint stripping waste, however, is covered in this study in Section 9.1.4.

9.1.3 Paint Application Waste

The wastes generated during paint application are primarily due to paint overspray or the failure of all of the paint to reach the target. If overspray did not occur, then no paint application waste would be generated and the need for equipment cleaning would be greatly diminished. Since the degree of overspray is a function of system design and operation, it can usually be reduced but never completely eliminated. The following source reduction measures are noted:

- Use of paint application equipment with low overspray values.
  When comparing different types of paint application equipment, the transfer efficiency or degree of paint overspray produced can vary considerably. Brewer (1980) lists the following efficiency ranges for several different spray systems:

Spray Method	Efficiency
Conventional air-atomized	30-60%
Conventional pressure-atomized	65-70%
Electrostatic air-atomized	65-85%
Electrostatic centrifugally-atomized	85-95%

  One company, Flexsteel Industries in Dubuque, Iowa, changed from a conventional spray system to an electrostatic system and reduced the amount of overspray it was generating by 40 percent (Campbell and Glenn

1982). This saved the company $15,000 a year in paint cost and repaid the investment within two years.

Other types of equipment that can yield even higher efficiency values are roller and flow coating machines (90 to 98 percent) and electrocoating systems (90 to 99 percent). Roller and flow coating machines, however, would be limited in their applicability based on the shape of the parts. Electrocoating systems would require a shift from solvent-based to water-based paint and is discussed in Section 10, Product Substitution. Other high efficiency systems, such as those that use powder coatings, are also discussed in Section 10.

- Better operating practices.

  Since many spray systems are manually operated, the equipment operator has a major impact on the amount of waste produced. D. Lenchkus (1982) reports that spray operators generally believe that a large amount of air is required to achieve proper atomization of the paint. When air pressures are set too high, the paint has a tendency to bounce off the surface and increase overspray. Overspray can run as high as 70 percent and achieving a level of 50 percent is rare. Another reported factor affecting overspray is the practice of arching the spray gun instead of keeping it perpendicular to the surface. When the gun is arched 45 degrees away from the surface at the end of each stroke, overspray can be as great as 65 percent and an uneven coat of paint can result. By providing the proper training for spray system operators, waste generation can be minimized. Manual operations have been eliminated altogether in many facilities with the use of robots.

  Preventive maintenance also plays a critical role in reducing the amount of overspray, stripping waste, and equipment cleaning wastes produced. Whenever a bad finish is produced, the paint is normally stripped off and the entire paint application procedure is begun again. By maintaining all application equipment in good working order, the likelihood of producing a bad finish is lessened. Spray guns should be cleaned after use or whenever there will be an appreciable interval between use. For hand-held units, a solvent rinse with occasional blow-back (cover the fluid tip and operate the

trigger; this blows the paint back to its container) is adequate. All moving parts should be lubricated frequently and properly adjusted. A spray gun should always be able to provide a smooth change from solid fan to round cone by adjustment of the controls.

Roller coating and flow coating machines must also be properly maintained if they are to produce good finishes. Rollers on roller coating machines should be cleaned regularly to remove dried paint and inspected for swelling of the material. If swelling is evident, the rollers should be replaced immediately. Curtain or flow coating machines have a curtain head that must be kept clear at all times. If this aperture becomes blocked, the curtain will break and give an uneven finish. To clean the machine, solvent should first be circulated through the machine. After this, the aperture should be fully opened and cleaned with a soft rag or brush. Metal instruments should never be used for cleaning the curtain head.

In addition, by fully inspecting parts before they are painted, the painting of potential rejects can be avoided. Whenever a part is painted and then rejected, additional stripping, cleaning, and painting wastes are generated. If potential rejects are discovered before painting, they can probably be corrected (cleaned if the problem is contamination) and then painted with very little increase in waste generation.

9.1.4 Paint Stripping Waste

Paint stripping is required whenever a bad finish is produced or when the old coating must be removed prior to re-painting. Reasons for bad finishes can include improper cleaning, improper paint application, or both. Since the need for paint stripping is based in parts, on the failure of other operations, some of the control methodologies are aimed at reducing the number of rejects produced. Source reduction methods considered for reducing wastes due to paint stripping are:

- Implementation of proper paint application techniques.
  By properly applying paint to a given surface, the likelihood of producing a bad finish is reduced. This, in turn, reduces the generation of waste

associated with paint stripping and repainting. Since the proper application of paint is based on the type of equipment used and the ways in which it is operated and maintained, the reader is referred to Section 9.1.3 for further information.

- Implementation of proper cleaning techniques.
  Proper cleaning requires the identification of the contamination, determination of the cleaning operations required to achieve a given degree of cleanliness, and the correct practice of these operations. In addition, proper design of the rinse systems is essential for achieving good cleaning and reducing the chance of cleaning solutions becoming unwanted contaminants. For an in-depth study of proper cleaning techniques, the reader is referred to the process study on metal parts cleaning.

- Use of mechanical paint stripping methods.
  Cryogenic paint stripping uses liquid nitrogen and plastic beads to embrittle and then remove layers of paint from an object. The Cryogenic Coating Removal (CCR) system consists of a feed system that propels non-abrasive plastic shot at a cryogenically-embrittled rotating target. Since the paint is under thermal tension, it debonds when impacted by the shot. From this system, the loose paint and shot are separated in a second system and the shot returned to the process. A full scale CCR system has been installed by a major domestic auto manufacturer and the results were impressive. Compared to hot caustic stripping, the operating costs were 44 percent lower; (this did not include accounting for increased parts damage and disposal costs due to the use of caustic). Recent tests have been successful on a wide variety of paints and thicknesses which makes CCR appear to be an attractive substitute system for conventional paint stripping operations.

For facilities handling items made of soft metals which are inappropriate for sand or glass bead blasting, plastic bead blasting appears to be an attractive option. Hill Air Force Base (AGB) in Ogden, Utah has used plastic bead blasting with great success (Higgins et al 1985). Previously, paint removal from aircraft was a time consuming and messy operation. Sprays or baths containing acidic methylene chloride, phenolic,

or hot alkaline sodium hydroxide solutions were used to soften the paint on the plane. Then the paint was scraped off and large volumes of water were used to rinse off the surface. The resulting rinsewater (tens of thousands of gallons per plane) had to be treated and the wet paint sludge disposed. The new system utilizes high pressure air to propel the plastic beads against the painted surface to dislodge the paint. Paint and plastic are then recovered and separated with the plastic beads being returned to the feed system. Plastic beads that have broken down due to attrition are removed and disposed of along with the chipped paint. As reported by a source with the U.S Department of Defense, plastic bead blasting for all DOD facilities would cost $13 million to install and result in an annual savings of $100 million. With regard to waste generation, the currently used wet process annually produces 7 million gallons of paint stripper waste and 100 million gallons of wash water nationwide in all DOD facilities. The new system would eliminate these wastes and produce 500 thousand pounds of dry waste (paint plus spent plastic beads) instead. Because of the favorable economics, many airlines are looking into this process and many small scale systems are available commercially (Forth 1985).

- Use of non-phenolic strippers.

  Several non-phenolic/non-acid paint strippers have been developed in recent years in response to the need to reduce toxicity associated with phenol and acid additives (such as cresolic acid). Comparisons between non-phenolic, non-acid brush-on strippers such as Sprazee (made by BASF) and T-5873 (made by Turco) and phenolic/non-acid strippers such as T-5469 showed that the non-phenolic/non-acid strippers could provide the same degree of removal power (Staebler, Jr. and Simpers 1983). The main disadvantage was that much more stripper was needed for a given percent removal and a longer contact time was required. Some of these disadvantages were eliminated when non-phenolic/acid strippers were tested.

- Better operating practices.

  In addition to the methods discussed in the study on metal parts cleaning, the following example of proper equipment layout and its effect on waste generation was identified. Solvent soak tanks should be located away from paint curing ovens to minimize the adverse effects of solvent on a painted

surface or item. At one facility, a halogenated solvent soak tank was located near a paint curing oven. Heat from the oven caused solvent to evaporate from the tank. Being heavier than air, the vapors settled to the floor and entered the oven. Inside the oven, the vapors contacted the open flame and broke down, forming hydrochloric acid. Since the hydrochloric acid vapor altered the cure rate of the paint being applied, all of the resulting finishes had to be stripped off and reapplied (Durney 1982).

9.1.5 Equipment Cleaning Waste

Regular cleaning of paint application equipment is required to ensure that the production of rejects is minimized. Cleaning is also required whenever a different batch of paint is to be applied, (so as to minimize paint contamination from a previous batch of paint), or whenever the equipment undergoes a period of nonuse. Since the need for equipment cleaning is directly tied to the paint application operation, all of the methods listed in Section 9.1.3 are applicable.

- Better operating practices.

  An aspect of good operating practice not discussed in Section 9.1.3 would be the effect of scheduling improvements on equipment cleaning waste generation. Since the need for equipment cleaning can be tied to the frequency of paint color or type changes and the periods of inactivity, proper scheduling of production runs could reduce the need for equipment cleaning. By producing large batches of similarly painted items instead of small batches of differently painted items, a large reduction in the need for cleaning can be achieved. Some reductions would also be possible by painting light-colored items first and then the dark-colored ones. The reverse method is used in the paint manufacturing industry to reduce the need for cleaning of mixing tanks.

  Another good operating practice would be to segregate all solvents used for equipment cleanup*. When a similar or compatible type of paint was going

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*Westinghouse Electric Corp. 1985: Personal communication.

to be used in the equipment, the waste solvent then could be used as thinner or makeup for the fresh paint. This method was identified in both the paint manufacturing and printing operations process studies.

9.2 Implementation Profile

The two main methods discussed for use by industries performing paint application would be to operate all equipment properly and to install high efficiency paint application systems. Proper operation of the equipment would require that companies provide thorough training for their employees and maintain the integrity of the equipment. No additional equipment would be required and the only technical obstacle would be lack of information. Installing high-efficiency paint application equipment would require many companies to modernize their facilities. In addition, many high-efficiency systems use water-based paints only, so that different paint formulations would be required. Currently, extensive development work is being performed to find water-based substitutes for solvent-based paints.

Very few of the proposed control methods would require large outlays of capital. Many of the methods could result in net savings by reducing the cost of raw materials and waste disposal. Even the installation of new high-efficiency equipment has often been cost-effective. Therefore, it is very unlikely that implementation of the methods discussed here would entail economic hardships for industry.

9.3 Summary

Table 9-1 presents summary data on paint application waste sources and control methods. The ratings shown in the table were based on review of the available literature. Based on the measures already undertaken in the paint application field to minimize waste, it is estimated that 48 percent (a current reduction index of 1.9) of the potential waste that could be generated has been eliminated. By implementing additional waste reduction measures or increasing the use of already implemented measures, the amount of waste currently being generated could be reduced by 28 to 43 percent (a future reduction index of 1.1 to 1.7) . The most effective measures for achieving this reduction would be to use proper parts cleaning techniques, provide better operator training, and install high efficiency paint application equipment.

TABLE 9-1 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR PAINT APPLICATION

Waste Stream	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Empty Containers	1 Implement better operating practices	1	2	3	2	4		1.5	1.5	1.5
	Overall	1.00	2.00	3.00	2.00	4.00	0.01	1.5	1.5	1.5
Parts Cleaning Wastes (*)	1 See study on Metal Parts Cleaning	---	---	---	---	---		2.0	1.2	1.9
	Overall	---	---	---	---	---	0.68	2.0	1.2	1.9
Paint Application Wastes	1. Use equipment with low overspray	3	3	4	2	2		2.0	1.0	
	2 Implement better operating practices	2	3	3	2	4		1.5	1.5	1.5
	Overall	2.50	3.00	3.50	2.00	3.00	0.06	2.0	1.3	1.5
Paint Stripping Wastes (*)	1 Implement proper painting techniques	2	3	3	2	3		1.5	1.1	
	2. Implement proper cleaning techniques	2	3	3	2	3		1.5	1.1	
	3 Use mechanical paint stripping system	2	3	4	1	2		1.0	1.5	1.5
	4. Use non-phenolic/non-acid stripper	1	1	1	1	1		0.3	0.2	
	5 Implement better operating practices	1	2	2	3	3		1.5	0.4	
	Overall	1.60	2.40	2.60	1.80	2.40	0.01	1.5	0.9	1.5
Equipment Cleaning Wastes (*)	1 Use equipment with low overspray	3	3	3	2	2		1.5	0.8	
	2 Implement better operating practices	2	3	2	2	4		1.0	1.0	1.0
	Overall	2.50	3.00	2.50	2.00	3.00	0.24	1.5	0.9	1.0
All Sources	All Methods						1.00	1.9	1.1	1.7

(*) These waste streams include listed "F" and/or "K" RCRA wastes

10. WASTE REDUCTION THROUGH PRODUCT SUBSTITUTION

The bane of many finishing departments using solvent-based paint application systems has been the increasingly high cost of meeting air and water quality regulations, as well as problems in the disposal of hazardous and flammable wastes. The conventional solvent-based systems for paint application often pose potential health hazards, due to the emission of toxic solvents and the disposal of a large amount of waste paint sludge. To minimize the quantity and toxicity of waste paint requiring disposal, new coating types have been developed which eliminate the hazardous components of the paint and also allow for maximum re-use of paint overspray, thus increasing the efficiency of the paint application process. These alternatives include the use of water-based, radiation-curable, or powder coating techniques.

10.1 Water-Based Coatings

Water-based coatings are paints containing a substantial amount of water (often as much as 80 percent) in place of the volatile solvent. The polymers used include alkyd, polyester, vinyl acetate, acrylic, and epoxies, and can be dissolved, dispersed or emulsified. These coatings are supplied as baking finishes, as well as air-drying formulations. One feature which makes water-based coatings attractive is that no major equipment changes are necessary to apply water-based coatings with solvent-based coating equipment. The main waste reduction advantage, however, lies in the ease of recovering paint overspray. Overspray from a water-based coating can be collected or captured with water in the spray booth. The solution can subsequently be concentrated and reused as paint again. In addition to substantial reductions in environmental hazards due to significantly lower air emission levels and smaller amounts of waste paint sludge generated, water-based coatings can also provide energy savings by making possible the recirculation of the hot air used to cure the paint. Water-based coatings have increasingly been used by industry as an alternative to solvent-based systems. For example, Emerson Electric Company has reported the use of a water-based electrostatic paint system in place of a conventional organic solvent paint system (Huisingh et al. 1985). This substitution has resulted in a number of favorable changes. These include:

- Improved quality of application.
- Decrease of down time from 3% to 1%.

- Reduction in generation of aromatic waste solvent by 95%.
- Reduction of paint sludge by 97%.
- Increase in efficiency with up to 95% recovery and reuse of paint.

The new system also reduced hazardous waste disposal costs and decreased personnel and maintenance costs by 40 percent.

10.2 Radiation-Curable Coatings

Another alternative to solvent-based coatings is radiation-curable coatings. These coatings do not contain or use organic solvents. Reactive monomers are applied as a liquid to a surface which is then exposed to high energy radiation such as UV or IR light. Radiation-curable coatings account for 12 to 15 percent of the curable coating market and were expected to capture 20 percent by 1985 (Campbell and Glenn 1982). The advantages of using this coating technique include the reduction in wastage from solvent loss and a substantial decrease in energy and maintenance requirements.

10.1.3 Powder Coatings

Powder coatings represent an attractive third alternative to solvent-based coatings. Use of powder coatings has been referred to as a "dry painting process". The process is simple in operation and can be done manually or by highly automated equipment. With manual systems, the powder is sprayed on the object and the overspray is readily retrieved and recycled. The unused powder is then collected and separated from an air stream by various vacuum and filtering methods. It is returned to the feed hopper for reuse. This ability to recycle the coating material provides a very high efficiency-use ratio. Powder coatings can also be effectively applied in a fluidized bed*. Since the system is entirely enclosed, there is no overspray to collect for the application area. Hence, the coating powder remains clean at all times and the potential for waste generation (contaminated powder) is nearly zero. Fluidized bed coating with powdered paint is a well-proven technology*.

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* Westinghouse Electric Corp. 1985: Personal communications.

Powder coatings fall into two broad categories - thermoplastic and thermosetting, the choice of which depends on the application. Powder coating still represents a small fraction (5 to 6 percent) of the U.S. industrial coating market, but its share is rapidly increasing. Better coating materials such as epoxy-polyester hybrids have been developed to improve film deposition characteristics and to allow for lower curing temperatures. Improvements in spraying equipment have also contributed significantly to the rapid spread of powder coating use for more than 200 different types of consumer and industrial products.

The greatest non-product advantage of using powder coating lies in the elimination of environmental problems inherently associated with most liquid-based finishing systems. Powder coatings contain no solvent and thereby emit negligible volatile organic compounds. Furthermore, since powder overspray can be readily recycled, material utilization is high and solid waste generation is minimal. Recent case studies are demonstrating that powder coating systems can be more efficient, cleaner, and more environmentally acceptable, while producing a higher quality finish in conventional solvent-based, water-based, or high solid compliance coating systems (Letsky 1960). A model study developed in 1982 (Cole 1984) showed that powder coating systems are economically feasible since the higher installation cost can be offset by lower maintenance, materials, labor/cleaning, energy, and waste disposal costs. Compared to solvent-based coatings, powder coatings provide a 90 percent waste reduction, reduce rejects by a factor of 4 or greater, and require 30 to 50 percent less energy and 30 to 40 percent less labor. However, the broader issue of the quantity and toxicity of wastes generated during the production (as opposed to application) of powder coatings was not addressed in this study.

Regulations dealing with control of volatile organic emissions have been a major motivating factor behind implementation of the product substitution alternatives described above. As stricter air quality standards and the costs for waste disposal escalate, the use of these substitutes will increase. Additional implementation will also occur as these products become proven in use and gain public acceptance. Since they all offer attractive economic incentives even when the effects of waste generation are ignored, their share of the product coatings market should increase steadily.

11. CONCLUSIONS

While the product coating industry has done much to reduce the amount of potential waste it could generate, it appears that further waste generation reductions are possible in the range from 28 to 43 percent. Several methods that generally appear to be most effective would be to emphasize proper cleaning techniques, provide better operator training, and install paint application systems with low overspray.

Three practiced product substitution alternatives were identified: water based coatings, radiation curable coatings and powder coatings.

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13. INDUSTRY CONTACTS

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PROCESS EQUIPMENT CLEANING

1. INTRODUCTION

Equipment cleaning is a periodic preventive maintenance function performed in order to remove an undesirable deposit (dirt, rust, scale, clingage, tars, etc.) from the internal surfaces of process equipment. Generally, equipment cleaning is performed for the following purposes:

- Maintain or restore the operating efficiency of the equipment.
- Extend the lifetime of the equipment by minimizing corrosion.
- Remove deposits to allow for inspection or repair of the equipment.
- Avoid or limit product contamination.

Equipment cleaning is widely practiced in all segments of the manufacturing industries. However, from the waste generation viewpoint, chemical processing and compounding operations are of special significance, due to the nature and amounts of cleaning wastes generated annually.

2. DESCRIPTION OF CLEANING TECHNIQUES

Usually, a distinction is made between chemical and mechanical cleaning. Chemical cleaning requires the use of chemicals, such as those listed in Table 2-1, which are employed to chemically attack the deposits and render them either water-or solvent-soluble. The basic removal mechanism is usually through oxidation, reduction, chelation, or conversion of insoluble oxides into soluble salts. Physical or mechanical cleaning relies on breaking the adhesion of the deposit to a surface through the use of mechanical devices such as scrapers, squeegees, rags, drag-lines, pigs, or through the use of high pressure liquid jetting or hydroblasting.

While other classifications of cleaning techniques are possible, the classification proposed by Loucks (1973) was adopted, resulting in the following six categories of cleaning techniques:

- "Fill and empty" technique
- "Circulation" technique

TABLE 2-1. SOME CHEMICAL CLEANING COMPOUNDS AND THEIR USAGE

Cleaning Compound	Chemical Action	Usage	Remarks
Hydrochloric Acid	Dissolves most water scales and corrosion products	Used on boilers, heat exchangers, pipelines, etc.	Corrosive to steel; temperatures must be below 175°F
Sulfuric Acid	Dissolves most corrosion products	Limited use	Cannot remove water scales
Nitric Acid	Same as HCl	Used for stainless steel and aluminum	Cannot be used for copper and ferrous alloys
Hydrofluoric Acid	Dissolves silicate deposits	Used as an additive to HCl (as ammonium bifluoride)	Very dangerous to handle
Sulfamic Acid	Dissolves calcium salts	Used as an additive to HCl	Easy to handle; soluble calcium salts
Citric Acid	Dissolves iron oxides	Used mostly to clean boilers Frequently with added ammonia and oxidizers	Not good for water scale removal
Caustic Soda, Soda Ash	Dissolves oil and grease	Used to remove oil and grease before acid cleaning and to neutralize the acid after cleaning	Dangerous to handle
Ammonia	Forms soluble complexes with copper ions	Used to remove copper from large boilers	Needs to be handled carefully
Ethylene Diamine Tetra-Acetate (EDTA)	Dissolves water scales at alkaline pHs	Used for cleaning water systems without shutdown	Expensive

Source: Boosting Capacities with Chemicals (Loucks 1973), Handbook of Industrial Water Conditioning (Betz 1980).

- "Flow-over" technique
- "Gas Propel" technique
- "Process Simulation" technique
- "Onstream Cleaning" technique.

These techniques are briefly described below.

2.1 "Fill and Empty" Technique

In this method, the process vessel is isolated from other equipment and filled with the appropriate cleaning medium. The solution can be heated and agitated to facilitate scale removal. After a period of time (usually four-to-eight hours for chemical cleaning), the solution is drained. Rinse water or diluted alkali or acid solutions can then be used to ensure complete removal of the cleaning chemical. The drained chemicals and the subsequent rinses are either reused, treated, recycled, or land-filled, depending on their composition and on the availability of options at the particular site. The drawbacks include the necessity to maintain large quantities of cleaning solution and relatively high equipment downtime.

2.2 "Circulation" Technique

Circulating or flow-through cleaning is usually performed on small vessels or equipment, such as heat exchangers. The vessel is filled with cleaning solution to an overflow line and allowed to stand for a short period of time. Fresh cleaning solution is then pumped in, while the used solution is displaced and routed to waste-disposal or returned to the pump to be recirculated. In large boilers, nitrogen gas is sometimes used to provide agitation for more effective scale removal.

2.3 "Flow-over" Technique

For larger vessels and storage tanks, cleaning by filling or recirculating requires too much cleaning solution. This equipment is cleaned by applying the cleaning liquid with spray jets and allowing the liquid to flow off.

2.4 "Gas-Propel" Technique

For cleaning agents that are not very corrosive steam can be used to propel them through the system. This technique is useful for pipelines, where fill-and-empty or circulating methods are less efficient. Here, inhibited organic acids or chelants are put in a flow of steam which carries the liquid drops and solid debris through the hydraulic obstacles of the system. This method is quick, efficient, and requires a minimum quantity of materials. At the end of the cleaning process, the system is dried by stopping the steam flow and blowing through with dry air or gas. This method can be used to clean large vessels when flow-over methods are not suitable. Sometimes, surfactants and air can be used with cleaning agents to make a low-density foam. This method is used mostly for cleaning the tube sides of large surface condensers.

2.5 "Process Simulation" Technique

For equipment that is easily fouled, two or more process units are usually provided in parallel. Such equipment is often cleaned by a simulated operation. Here, the unit is isolated from the process and the process stream is replaced by a cleaning fluid, with the system's pumps and temperature control still in operation. An example of this operation is the removal of iron oxides and copper from high-pressure steam generators using ammoniated ethylene-diamine-tetra-acetate (EDTA).

2.6 "Onstream Cleaning" Technique

The ideal way to clean any equipment is to do so when it is in normal operation. Chelants such as EDTA, when added to the process stream, can dissolve deposits. This technique is used for cleaning reactor jackets, large gas-compressor-station engines, closed circuit heating and air conditioning systems, etc. In-service cleaning of large circulating water cooling systems is done through intermittent pH control - to the acid side of neutral and back again.

On-stream cleaning is also accomplished with mechanical devices, e.g., rod-out of process connections with ram valves, or heat exchanger tube cleaning using moveable tube insert brushes propelled by process fluid.

3. WASTE GENERATION ASPECTS OF EQUIPMENT CLEANING

The composition and quantity of cleaning wastes differ widely depending on:

- Type of deposit being cleaned.
- Type of cleaning fluid.
- Type of cleaning method.
- Size of equipment being cleaned.
- Cleaning frequency.

In general, batch operations generate more cleanup waste than continuous processes. This is mainly because of the higher cleanup frequency associated with utilizing the same equipment (typically a mix tank or an autoclave), for batch production of differing materials. For example, in plasticizer manufacturing, the same jacketed kettle reactor is often used for different esterification reactions to produce a large variety of esters of phtallic, trimellitic, adipic, sebacic, stearic or oleic acids. The changeover from production of one type of chemical to another requires cleaning of the reactor internals. By contrast, equipment used in the continuous processes (e.g., vinyl chloride monomer manufacture), is cleaned once every one or two years during a scheduled plant maintenance shutdown period.

In batch operations, such as in paint manufacturing, food processing, or fermentation, where cleanup frequency is high and the cleaning solution inventory is large, it is a standard practice to provide "clean-in-place" (CIP) systems. Such systems consist of stationary spray head manifolds inside the production vessels, effluent piping, tankage, heat exchangers, pumps, solids separation equipment, distribution systems for solution re-use, and chemical dosing units. Minimization of cleaning solution use through counter-current staging of rinse operations is especially attractive for large integrated CIP systems.

Waste generation by equipment cleaning operations generally can be addressed by examining cleaning operations performed on various process equipment. The following sections deal with the cleaning of specific process equipment.

3.1 Batch Reactors and Mixers

Batch reactors or mixers are cleaned to remove material that adheres to the vessel walls (clingage). This is done to ensure product purity of the subsequent batch and to prevent clogging of the outlet connections. Clingage problems dominate in the industries where batch polymerization is performed (plastic, resins, synthetic rubber), in the paint manufacturing industry (where equipment cleanup waste associated with clingage removal is a major waste stream), in paint application throughout the industrial sector, and in specialty chemicals manufacturing, where batch processing is prevalent.

3.2 Tanks and Containers

Tanks and containers are used for storage of process inventories and must be periodically cleaned to prevent accumulation of contaminants or to remove sedimented solids. Tank cleaning is typically performed using the flow-over method, because of the large surface areas involved. Small vessel cleaning is done using circulation or fill and empty techniques.

3.3 Heat Transfer Equipment

Heat exchanger fouling is a commonly encountered problem caused by the formation of deposits on heat transfer surfaces. These deposits decrease heat transfer efficiency and increase pumping energy requirements. Deposits form through precipitation of insoluble substances which adhere to the exposed heat exchange surfaces. The rate of deposit formation depends on the nature of the fluids, film temperatures, turbulence, and the smoothness of the metal surface. Fouling deposits are removed periodically to restore heat transfer efficiency, decrease hydraulic resistance, and, in some cases, circumvent corrosion. Cleaning is usually done by one of two methods - hydroblasting or chemical cleaning (VanMatre, 1977).

Hydroblasting uses high pressure water jets to remove water scale deposits. This cleaning procedure involves the dismantling of the heat exchanger. The shell side scales are removed by using the "bundle blaster", which is usually equipped with cleaning heads that rotate 90 degrees. The tubeside scales are removed by using the "lancing machine", which employs stabbing devices that drive in and out of the tubes. The advantages of

hydroblasting are that the results are easily inspected and corrected, if necessary. The disadvantages of this technique are that the equipment is out of service for a long period of time, and that dismantling involves high labor costs.

Chemical cleaning involves the use of chemicals, as discussed in Section 2, mainly to remove water scale deposits. In some instances, chemical cleaning can be done with the equipment still on stream, as discussed in Section 2.6. Though on-stream cleaning is generally not as effective as out-of-service cleaning, reduction in the equipment downtime offers an economic incentive.

4. WASTE REDUCTION THROUGH SOURCE CONTROL

4.1 Description of Source Control Techniques

The problem of waste minimization associated with process equipment cleaning can be addressed using two distinct approaches:

- Reducing the frequency of cleanups
- Reducing the quantity and/or toxicity of wastes.

The first approach relies on reducing the need for cleaning. The second approach deals with how to reduce wasteloads associated with the cleaning process when it has to be performed. In the following sections, both approaches are discussed.

4.1.1 Reduction of Cleanup Frequency

Reduction (or elimination) of the need for cleaning is accomplished by identifying the causes of undesirable deposit formation, followed by identifying and implementing the means to prevent or limit deposit formation. Discussion is provided below of the following measures:

- o Proper plant and equipment design
- o Recognition of cleaning costs as a separate item
- o Conversion from batch to continuous process
- o Maximizing dedication of process equipment
- o Avoidance of unnecessary cleaning
- o Inhibition of fouling deposit formation rate.

Identified case examples are provided where applicable.

- Proper plant and equipment design.
  Cleaning considerations are, (or should be), an integral part of the plant and equipment design. Typically, these considerations encompass avoidance of undrainable pockets and minimization of equipment or piping surfaces exposed to the process fluid.

- Recognition of cleaning as a separate item by management.
  Often the costs of cleaning are lumped together with other maintenance costs, thus losing their identity and visibility to management. Without a proper identification of the overall magnitude of these costs and the various individual cleaning cost elements, the analysis of alternatives to frequent cleaning cannot be meaningfully performed.

- Conversion from batch to continuous process.
  Such a conversion, where possible, will reduce cleaning wastes for the reasons discussed in Section 3. The additional benefits of the continuous process include lower labor requirements, ease of automation and control (which minimizes human error leading to inferior quality products), and the elimination of the need for manual material transfer operations characterized by a high probability of spillage.

  Historically, the changeover from batch (or cyclic) to continuous operations has been very common in the chemical industry because of technological progress and increased product demand (Peters and Timmerhaus 1980). However, in certain cases, batch operations have proven advantageous over continuous processing schemes. Here, the examples include the development (but not the widespread use) of continuous processes for neoprene rubber manufacture (Anon. 1965, Euleco 1975) and for phenolic resins manufacture (Aho 1958, SIR 1968). It must be noted that the choice between batch and continuous operations is governed primarily by other factors than by waste generation. Common considerations include product diversity at the site, production volume, capital equipment cost, and operating cost.

- Maximizing dedication of process equipment.

  Making the process equipment more dedicated to a single product line or a single process function will generally reduce the need for frequent cleaning. This is typically accomplished through careful scheduling of production or by providing more specialized equipment. Both routes are extensively practiced in industries such as paint manufacturing and specialty chemicals manufacturing. Producers of specialty chemicals and formulations generally use batch processes with a number of similar products made in the same equipment. By proper scheduling, entire year supplies of individual products can be made in one campaign minimizing the numbers of changeovers and the down-times involved. Generally, the volumes of the specialty products produced are too low to justify continuous process equipment. Individual plant production volumes for such specialty items may range from 10 to 300 tons per year and volumes produced per batch may range from 1 to 10 tons.

  Generally, equipment utilization strategies and the resulting production schedules for batch processing are a product of optimization analysis, which maximizes the production rate with due consideration of such constraints as equipment cost (size) and availability, equipment downtime, labor cost and availability, length of operation(s), ancillary equipment availability, cost of cleanup, and cost of raw material losses. General descriptions of optimum strategy formulation are available (Peters and Timmerhaus 1980). Based on interviews with people who have had experience in the preparation of production schedules, formal optimization methodologies are not invoked often. Rather, a "common sense" approach based on trial-and-error is more widely used.

- Avoidance of unnecessary cleaning

  At times, equipment cleaning is performed routinely with little consideration for the rationale. In one actual case, a ball mill was used once every week to wet-grind a certain powder. The ball mill, with corrosion-proof internals, was totally dedicated to a single powder formulation, yet for no apparent reason, it was cleaned after each batch. The only justification provided was that other non-dedicated ball mills at the facility were cleaned after every use. In another example from the food processing industry, cleaning of the equipment,

in some instances, can be avoided, if the equipment can be adequately sanitized by heating.

o Inhibition of fouling deposit buildup rate

Fouling rates have been extensively studied and are usually attributed to the following processes (or their combination):

- Crystallization.
- Sedimentation.
- Chemical reactions and polymerization.
- High temperature coking.
- Corrosion.
- Bacterial growth.

Inhibition of fouling is of particular importance to heat transfer, where fouling associated with tars and scale formation is frequently experienced. Inhibition (slowing down) of buildup formation rates will reduce the cleaning frequency while improving the overall operating efficiency (i.e., heat transfer rate and hydraulic resistance). In general, the fouling deposit formation can be slowed down by the following measures:

- Use of smooth heat transfer surfaces.
- Lower film temperatures or increased turbulence.
- Control of stream composition.
- Choice of heat exchanger type.

The use of smooth heat transfer surfaces relies on reducing the adhesion between the deposit precursor and the heat transfer surface. The use of electropolished stainless steel tubes in a black liquor forced-circulation evaporator (used in the pulp and paper industry), resulted in a dramatic reduction of cleaning frequency from a period of once-a-week to once-a-year (Uddeholm Co., Tubec Tubes Brochure). Smooth non-stick surfaces can also be provided by using Teflon*. Complete Teflon heat exchanger designs are available (DuPont 1985). The additional advantage of Teflon tubes is their ease of cleaning and corrosion resistance.

*Registered trademark of E.I. Du Pont Company.

For the heat exchangers, the fouling rate can be inhibited by lower film temperatures through the use of additional surface area and/or increased turbulence (high velocities). Avoidance of excessive overdesign and maintenance of sufficient velocity (e.g. through recirculation) during turndown operation will lower fouling rate and resulting cleaning frequency of heat exchangers (Garrett-Price 1985).

Inhibition of fouling rates can also be accomplished through prior removal of deposit precursors. Such inhibition can be achieved by early addition of polymerization inhibitors in monomeric resin manufacture. Other cleanup frequency reduction measures exist, such as application of less corrosive and more thermally stable heat transfer fluids and better design and/or control of fired heaters.

For closed cooling water systems, the fouling rate can be inhibited by proper water treatment, which includes pH control, hardness removal and dosing with biocide and corrosion inhibitors. Additionally, fouling rates can be controlled by lowering the number of concentration cycles in the cooling tower and by using make-up water with low total solids content. In certain applications, e.g., heating or cooling of slurries where deposit buildup due to sedimentation can be significant, the choice of heat exchanger type becomes important. For example, in fermentation plants, spiral plate heat exchangers are often used in preference to the shell-and-tube design because of the spiral plate exchanger's lower pressure drop and more favorable solids re-suspension, or non-plugging characteristics.

Slowing down of the deposit buildup rate is not only limited to heat transfer equipment, but is also important in crude oil storage tanks and crude desalting units. Crude oil's exposure to air can cause formation of gums and resins during long exposure periods inside storage tanks. Use of nitrogen blanketing or floating roof tanks has been suggested as a means of minimizing deposit formation due to air oxidation (Jacobs 1979), along with the removal of sludge-forming impurities prior to storage. Similarly, in the manufacturing exposure to air causes the formation of solid films that strongly adhere to the internal surface of the mixers. This can be avoided by using closed storage

and transfer systems . For example, Ford Motor Company modified their paint storage and transfer system to be totally enclosed with full recirculation, resulting in less frequent and easier cleanups and improvement in paint quality (Colleta and Bowers 1981). Other applications include coating of the reactor internals with special chemicals to prevent scale formation. These practices were reported in the suspension polymerization process for polyvinyl chloride manufacture (Cameron et. al 1980) .

4.1.2 Reducing the Quantity and Toxicity of Cleanup Waste

When equipment must be cleaned, the cleanup should be performed efficiently with a minimum generation of hazardous waste. Generally, the following considerations should be emphasized:

- The amount of clingage (or deposit) should be minimized.
- The amount of cleaning solution should be minimized, especially if it is expensive and/or hazardous.
- The choice of the cleaning medium should favor possible re-use or recycle, or result in the least toxic waste.
- Disposal of cleaning waste must be done in an environmentally acceptable fashion.

The sections below address each of the above aspects, except the last item (environmentally acceptable disposal), which is outside the scope of this study. Case examples found in the reviewed literature are also provided.

- Minimizing clingage

  The importance of minimizing clingage can be illustrated by waste generation in the paint manufacturing industry. Following pigment dispersion, a batch of paint is emptied from the mixer tank, leaving behind a residual layer (clingage) which adheres to the interior surface. The tank can then be cleaned using a caustic rinse and the resulting solution allowed to settle. The sludge is then removed and sent to land disposal with or without additional dewatering. It is clear that the ultimate quantity of sludge generated depends on how much residual paint was left in the tank. To reduce clingage, the following measures should be considered:

- Provision of adequate drainage time.
- Provision of non-stick surfaces, e.g., Teflon.
- Use of mechanical wall wipers (dual shaft mixers).
- Use of manual wall wipers (squeegees).
- Choice of cylindrical tanks with height-to-diameter ratio close to 1 in order to minimize wetted surface.
- Maximizing batch size.

All of the above measures are self-explanatory and do not require elaboration. All are practiced extensively throughout industry. The use of tank linings as means of reducing adherence and preventing corrosion has been addressed (Zolin 1984, Kays 1977). Use of dual shaft mixers with a slow scraper blade wiping the walls and the bottom of the mixing tank is common in applications involving viscous liquids*. Manual wipers are widely used in the cleaning of smaller portable tanks in the paint industry (see the process study elsewhere in this appendix on Paint Manufacturing).

o Minimizing the amount of cleaning solution.

The use of chemical cleaning (e.g., with mineral and organic acids) results in appreciable quantities of hazardous cleaning wastes which should be treated prior to land disposal. As appropriate treatment facilities are not readily available in every case, mechanical cleaning such as hydroblasting appears preferable over chemical cleaning. When chemical cleaning has to be used (for example, in cleaning of water scales from heat transfer surfaces), it is important to give preference to "flow-over" methods which require less solution than "fill-and-empty" methods (See section 2.)

When cleaning chemicals are used, there are generally four parameters that must be controlled: time, temperature, concentration, and turbulence. By using higher values of these parameters, the amount of cleaning chemicals can be reduced.

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* Myers Mixing Company, Montebello, CA 1985: Personal communication.

Adding proper additives to the cleaning agents will also result in a more efficient cleanup. By adding wetting agents, the cleaning chemicals can penetrate the scales more easily. Defoamers can be added to prevent the spillage of soapy bubbles, which form due to the presence of wetting agents. Suspending agents and emulsifiers can be added to prevent the settling of the soil and non diffusing liquids, respectively.

The use of clean-in-place (CIP) systems generally reduces the usage of the cleaning medium. This is especially effective when coupled with high velocity automated spray manifolds, and staged or counter-current rinsing. According to one source (USEPA 1979), an 80-90 percent reduction in aqueous solution use was achieved by installation of high pressure spray nozzles for tank rinsing in the paint industry.

In another example, a considerable reduction of toxicity of the reactor cleanup waste in phenolic resin manufacture was achieved by Borden Chemical (Huisingh et. al. 1985), where a two-step rinse sequence was employed. The first rinse was done with a small amount of water and therefore generated a concentrated stream which could be recycled to the process. The second, full volume rinse, generated wastewater with a much lower content of toxic material then the original method.

The ultimate approach to cutting down on the use of cleaning solutions is their elimination altogether. This is done by cleaning the equipment on-stream using mechanical devices. One example is provided by the use of "pigs" (contoured plugs propelled by the process liquid) to clean pipelines. Another example is a commercial system which uses steel brushes fitted inside heat exchanger tubes which are propelled by process fluid and reversed periodically by a flow divertor (WSA 1985).

- Choice of cleaning medium and cleaning solution reuse.
  From the waste generation standpoint, the hierarchy of cleaning medium choices appears to be process fluid over water over chemical solutions. Process fluids can be and are used to clean deposits. This choice is favored by the fact that following a simple filtration to separate out the solids, the

cleaning solution can be re-used as part of the formulation or process make-up stream. Examples include re-use of rinsewater from latex tank cleaning as part of latex formulation (Riley 1974), and the use of warm oil cleaning of crude oil storage tanks (Barnett 1980). The last example deserves more description. The sludge sediment in the crude oil storage tanks contains large quantities of entrapped oil (60 to 90 percent oil by volume). In the application described, a light gas oil, clean light crude stock, or other available low viscosity straight run distillate is warmed, mixed with dispersant additive, circulated through a tank to re-suspend the sludge and dissolve the oil, and is then sent to the refinery's slop oil recovery system where the oil is recovered and solids are efficiently separated. Previously used cleaning procedure relied on direct mechanical removal of sludge from the tank. Whereby large quantities of oil were lost and much higher waste quantities were produced.

4.2 Summary and Assessment of Source Control Techniques.

The techniques described in this report are summarized in Table 4-1. The compendium of methods presented, of course, is not complete by any means. Apart from its possible use as a guideline, it serves mainly to categorize various approaches and provide descriptions of and references to their known applications. To assess the overall potential and extent of possible future reductions of wastes generated in cleaning operations, along with the current extent of waste reduction achieved, each of the methods listed in Table 4-1 was rated on an integer scale of 0 (lowest) to 4 (highest) in the following three categories:

- Effectiveness in reducing waste.
- Extent of current use in the chemical processing industry.
- Future application potential.

Based on the ratings, the current and future waste reduction extents were computed, using the methodology described in the introduction to this appendix. The results are presented in Table 4-2.

5. CONCLUSIONS

It appears that waste reductions on the order of 18 to 35 percent can be achieved in the area of process equipment cleaning. This is shown by the future waste reduction index of

Table 4-1. Methods to Reduce Generation of Waste from Process Equipment Cleaning Operations

Approach	Method
Reduction of Cleaning Frequency	Proper plant and equipment design Recognition by management of cleaning costs as a separate item Conversion of process from batch to continuous or semi-continuous. Maximizing dedication of process equipment. Avoidance of unnecessary cleaning. Inhibition of fouling deposit formation through: - Use of smooth heat transfer surfaces (electropolished or Teflon tubes) - Lower film temperatures or increased turbulence. - Control of stream composition. - Choice of heat exchanger type.
Reduction of Quantity and/or Toxicity of Cleanup Wastes	Minimizing clingage through: - Provision of adequate batch drainage time. - Provision of non-stick surface. - Use of mechanical or manual wall wipers. - Choice of cylindrical tanks with low height-to-diameter ratio. - Agitator rotation after batch dump. - Maximizing batch size. Minimizing the amount of cleaning solution through: - Use of high pressure spray nozzles. - Use of "flow-over" technique. - Use of on-stream mechanical cleaning. - Use of clean-in-place systems with staged or counter-current rinsing. Choice of cleaning medium and cleaning solution reuse - Process fluid over hydroblasting over chemical cleaning. - Reuse of cleaning fluid.

TABLE 4-2 SUMMARY OF SOURCE CONTROL METHODOLOGY FOR PROCESS EQUIPMENT CLEANING

Approach	Control Methodology	Found Documentation		Waste Reduction Effectiveness	Extent of Current Use	Future Application Potential	Fraction of Total Waste	Current Reduction Index	Future Reduction Index	
		Quantity	Quality						Probable	Maximum
Reduce Cleaning Frequency	1. Proper plant and equipment design	1	2	2	2	1		1.0	0.3	
	2 Cleaning cost as a separate item	1	2	3	1	2		0 8	1.1	1.1
	3. Convert batch to continuous process	2	1	3	3	1		2.3	0.2	
	4 Maximize dedication of equipment	1	2	3	2	2		1.5	0.8	
	5 Avoid unnecessary cleaning	1	2	4	3	3		3.0	0 8	
	6 Use smooth heat transfer surfaces	2	2	3	1	2		0.8	1.1	1 1
	7 Lower film temp & increase turbulence	2	3	2	3	2		1 5	0.3	
	8 Control stream composition	3	3	3	3	3		2.3	0.6	
	9. Choice of heat exchanger type	1	2	2	3	3		1 5	0.4	
	Overall	1 56	2 11	2 78	2 33	2.11	0.50	3.0	0.6	1.1
Reduce Quantity and/or Toxicity of Cleanup Wastes	1. Adequate batch drainage time	0	2	1	3	2		0.8	0.1	
	2 Use non-stick surfaces	1	1	2	1	2		0.5	0.8	
	3. Use mechanical/manual wall wipers	2	2	3	2	3		1.5	1.1	
	4 Use tanks with low L/D ratios	0	2	2	2	1		1.0	0.3	
	5 Agitator rotation	1	1	1	2	2		0.5	0.3	
	6 Maximize batch size	0	2	2	3	2		1 5	0.3	
	7. Use high pressure spray nozzles	2	2	3	2	3		1.5	1 1	
	8 Use "flow-over" techniques	1	2	3	2	1		1.5	0.4	
	9 Use on-stream mechanical cleaning	2	2	3	1	3		0.8	1.7	1 7
	10 Use CIP system with staged/CCD rinses	2	2	3	2	2		1.5	0.8	
	11. Proper cleaning medium choice	1	2	3	2	2		1.5	0 8	
	12 Reuse of cleaning fluids	1	2	4	1	2		1.0	1.5	
	Overall	1.08	1 83	2 50	1.92	2.08	0.50	1 5	0.7	1.7
All Sources	All Methods						1 00	2.6	0.7	1.4

0.7 to 1.4 on scale of 0 to 4. However, the current reduction index of 2.6 is indicative that significant waste reduction has already been achieved, due to partial implementation of the techniques summarized in Table 4-2.

Of the 19 techniques listed, the use of smooth heat exchanger surfaces, on-stream mechanical cleaning and cleaning fluid re-use appear to be most attractive for future applications as evidenced by high future reduction indices.

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