THE PRODUCT SIDE OF POLLUTION PREVENTION:

EVALUATING THE POTENTIAL FOR SAFE SUBSTITUTES

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FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. These laws direct EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for planning, implementing, and managing research, development and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This report, *The Product Side of Pollution Prevention: Evaluating the Potential for Safe Substitutes*, funded through the Pollution Prevention Research Branch, is a major project in the area of the Cleaner Products Program in researching methods to support the design and development of products whose manufacture, use, recycle and disposal represent reduced impacts on the environment.

This report is an in-depth study of the potential for substituting safer or less toxic chemicals for seventeen of the priority 33/50 chemicals from the Toxic Release Inventory. Chemical use trees have been developed to display the primary uses and products manufactured from these chemicals. From these chemicals use trees, seven priority product categories have been developed and each of these categories is researched to provide timely information on current releases, status of the manufacturing and projections of possibilities for safer chemical substitutions and therefore source reduction of toxic chemical releases to the environment. Product design from manufacturing, to marketing and ultimate disposal is an integral component of the equation for innovative source reduction and responsible waste management. The reader is encouraged to contact the authors or project officer for more information concerning this project and report.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

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ABSTRACT

The hazardous waste problem and many of the persistent air and water pollution problems are primarily toxic chemical problems. Widespread use of toxic chemicals in industry and commerce has created the need to deal with toxic releases into the air, water and contained in soil. Regulations have not sufficiently reduced environmental releases nor have they protected workers for effects of these toxic agents in the workplace or consumers from toxic chemicals found in products. Substitution of products and practices reducing use of toxic chemicals can reduce hazardous waste generation, mitigate toxic air and water pollution and reduce worker exposure and public exposure to toxic chemicals.

This report presents results to evaluate the possibility of dramatic reductions in toxic chemical releases by focussing on safe substitutes for products that contain or use toxic chemicals in their manufacturing process. Identifying priority products for substitution and evaluating the feasibility of safe substitutes for those products is an important step in the shift toward prevention of toxic chemical pollution at the source.

This report illustrates that the generation of hazardous waste and toxic pollutants is the choice made in the design of products and by the manufacturing processes in their production. It evaluates the potential for safe substitutes for priority uses of toxic chemicals by identifying and evaluating priority products that contain or use certain priority chemicals in their production; by identifying the existing substitutes for these priority products; and determining the technical impediments to the use of safe substitutes for priority products. Future research needs are also identified and a method is presented for identifying priority chemicals for substitute evaluation.

This report was submitted in partial fulfillment of Cooperative Agreement CR #816735-01-0 by the University of Tennessee's Center for Clean Products and Clean Technologies, under the sponsorship of the U.S. Environmental Protection Agency. This work covers a period from September 10, 1990 to September 9, 1994, and was completed as of August, 1994.

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ACRONYMS and CHEMICAL ABBREVIATIONS

Ag_2O	silver oxide
Al	aluminum
APS	aqueous powder suspension
ASF or A/ft^2	amperes per square foot
ASTM	American Society of Testing and Materials
atm	atmospheres
BOD	biological oxygen demand
BTX	benzene, toluene, and xylene
CAA	Clean Air Act
Cd	cadmium
CFC	chlorofluorocarbon
CFM	chloroform
Cl_2	chlorine
CN	cyanide (CN-, cyanide moiety)
CNS	central nervous system
Co	cobalt
CO_2	carbon dioxide
Cr	chromium
Cr(III)	trivalent chromium
Cr(VI)	hexavalent chromium
CrO_3	chromic trioxide
CTC	carbon tetrachloride
CTSA	Cleaner Technology Substitutes Assessment
DBE	dibasic ester
DCM	dichloromethane or methylene chloride
DfE	Design for the Environment
DMT-PTA	dimethyl terephthalate and terephthalatic acid
DOE	Department of Energy
EDC	ethylene dichloride
EPA	Environmental Protection Agency
FAA	Federal Aviation Association
FDA	Food and Drug Administration
gal	gallons
g/l	grams per liter
GNP	gross national product
GSA	General Services Administration
HAP	hazardous air pollutant
H_2CrO_4	chromic acid
HCFC	hydrochlorofluorocarbon
HCl	hydrogen chloride
HCN	hydrogen cyanide
Hg	mercury
HgS	mercury sulfide ore, or cinnabar
KOH	potassium hydroxide
$LaNi_5$	lanthanum nickel alloy
lbs	pounds
lbs/yr	pounds per year

Li-CF	lithium-carbon monofluoride
Li-FeS$_2$	lithium-iron disulfide or lithium-iron pyrite
Li-I$_2$	lithium-iodine
Li-MnO$_2$	lithium-manganese dioxide
Li-SO$_2$	lithium-sulfur dioxide
Li-SOCl$_2$	lithium-thionyl chloride
MEK	methyl ethyl ketone
mg/l	milligrams per liter
mg/m^3	milligrams per cubic meter
MIBK	methyl isobutyl ketone
m^3	cubic meter
Mm	misch metal
mm	millimeter
MMA	methyl methacrylate
Mn	manganese
MnO$_2$	manganese dioxide
MSDS	material safety data sheets
NaCN	sodium cyanide
NaS	sodium-sulfur
NESHAP	National Emission Standard for Hazardous Air Pollutant
Ni	nickel
NiCd	nickel-cadmium
NiFe	nickel-iron
NiMH	nickel-metal hydride
NiZn	nickel-zinc
NMP	n-methyl pyrrolidone
NPRC	National Polystyrene Recycling Company
NSPS	New Source Performance Standards
OEM	original equipment manufacturing
OPPT	Office of Pollution Prevention and Toxics
OSHA	Occupational Safety and Health Administration
Pb	lead
PbS	lead sulfide ore, or galena
PCE	tetrachloroethylene or perchloroethylene
PEL	permissible exposure limit
PET	polyethylene terephtalate
PHB	poly(hydroxybutyrate valerate)
	polylactic acid or polylactace
POTW	publicly owned treatment works
ppb	parts per billion
ppm	parts per million
PSES	pretreatment standards for existing sources
PVC	polyvinyl chloride
RCRA	Resource Conservation and Recovery Act
RON	research octane number
SIC	standard industrial code
SLI	starting, lighting, and ignition
TCA	1,1,1-trichloroethane
TCE	trichloroethylene

TRI	Toxics Release Inventory
U.S.	United States
UST	underground storage tanks
VOC	volatile organic compound
°C	degrees Celsius
$/lb	dollars per pound

INTRODUCTION AND EXECUTIVE SUMMARY

INTRODUCTION

The hazardous waste problem and many of the persistent air and water pollution problems are primarily toxic chemical problems. Widespread use of toxic chemicals in all segments of industry and commerce has created the need to deal with burgeoning wastestreams containing toxic chemicals emitted into the air and water and buried in the soil. Two decades of pollution control regulations have not sufficiently reduced environmental releases of toxic chemicals to acceptable levels. Nor have regulations always protected workers from the effects of toxic chemicals used in the workplace or consumers from the effects of toxic chemicals found in consumer products.

> *Substitution of products that do not require the use of toxic chemicals can reduce hazardous waste generation, mitigate toxic air and water pollution, and reduce both worker and public exposure to toxic chemicals.*

Substitution of products (and, in some cases, practices) that do not require the use of toxic chemicals can reduce hazardous waste generation, mitigate toxic air and water pollution, and reduce both worker exposure to toxic chemicals and public exposure to toxic products. Furthermore, as many companies have already discovered, safe substitutes save money that would otherwise be spent on environmental controls, penalties, cleanup costs, and worker health care.

This report presents the results of the first study to evaluate the possibility of dramatic reductions in toxic chemical releases by focussing on safe substitutes for products that contain or use toxic chemicals in their manufacturing processes. By identifying priority products for substitution and evaluating the feasibility of safe substitutes for those products, this study provides an important step in the shift toward prevention of toxic chemical pollution at the source.

During the time in which this project has been conducted, the shift toward prevention of toxic chemical pollution at the source has been taking

place, often at a pace that would have seemed impossible a few years ago. Major efforts have been initiated by the United States Environmental Protection Agency (EPA) and other federal and state agencies to explore the use of safe substitutes for priority toxic chemicals that far surpass this modest first study in resources and industry participation. The chlorofluorocarbon substitutes evaluations initiated by the Clean Air Act Amendments of 1990, the EPA sponsored Cleaner Technology Demonstrations for 33/50 Chemicals, and the EPA Design for the Environment Program are only three examples of these major efforts.

> *This report is intended to illustrate that the generation of hazardous waste and toxic pollutants is the result of choices made in the design of products and the processes by which they are made.*

Another shift that has taken place during the period of this study is the use of the life cycle concept and the methodology of life cycle assessment to evaluate the relative environmental impacts of products. The life cycle concept includes an assessment of not only the direct impacts of toxic chemical exposure but other major impacts, such as global climate change, acid rain, ozone depletion, and resource depletion. The life cycle concept and the methodology of life cycle assessment are similar to the approach used in this study in that they look at the whole manufacturing process for products and not just at the products themselves. The life cycle concept and the approach used in this study place the use of toxic chemicals in the context of whole product systems in order to illuminate patterns of materials use and environmental impacts that

are not readily seen when focussing on one product or one chemical use.

This report is first intended to illustrate that the generation of hazardous waste and toxic pollutants is the result of choices made in the design of products and the processes by which they are made that require the use of toxic chemicals. These choices were not made lightly in most cases. The chemicals chosen that are now priority pollutants have properties that make them well suited for their uses. The web of production of numerous products and materials that consumers have come to depend upon is based in large measure on toxic chemicals discussed in this report that have become industrial building blocks. These products and materials include plastics and synthetic fibers, electronics components and batteries, paints and coatings, and plated metal materials used in automobiles and household appliances.

> *The idea of safe substitutes and the research in this report challenge the necessity of massive toxic chemical releases while recognizing that there are no across-the-board solutions and that each chemical use is unique.*

This dependence on hundreds of uses of building block toxic chemicals has become so pervasive that their release to the environment by the millions of pounds is accepted as a necessity of this industrial economy. The EPA's 33/50 Program of voluntary reductions in the releases of priority toxic chemicals was a positive challenge to this acceptance. The idea of safe substitutes and the research in this report also challenge the necessity of massive toxic chemical releases while recognizing that there are no across-the-board solutions and that each chemical use is unique.

> *A concerted effort to develop safe substitutes for major uses of priority toxic chemicals, through product and process redesign, can reduce hazardous waste generation and toxic chemical pollution without sacrificing the functions of goods and services that society has come to rely upon.*

With the relatively modest level of effort of this exploratory project, existing substitutes for priority toxic chemicals were identified that can result in dramatic reductions in the releases of these toxic chemicals. Many of these are now coming into wider use. A concerted effort by manufacturers, with EPA leadership, to develop safe substitutes for major uses of priority toxic chemicals, through product and process redesign, can reduce hazardous waste generation and toxic chemical pollution without sacrificing the functions of goods and services that society has come to rely upon.

OBJECTIVES OF THE PROJECT

The objectives for this study were to:

1) evaluate the potential for safe substitutes for priority uses of toxic chemicals by:

■ identifying priority products that contain or use certain priority chemicals in their production;

■ identifying and evaluating the existing substitutes for these priority products; and

■ determining technical impediments to the use of safe substitutes for priority products.

2) Determine the future research needs for safe substitutes for priority products; and

3) Develop a method for identifying priority chemicals for substitute evaluation.

APPROACH

The identification of priority products for substitution starts from the perspective of priority chemicals. Priority products include products that either contain priority chemicals or somehow incorporate them in the manufacturing process in a way that results in environmental releases or worker exposure. By reducing the use of these priority products, the uses and releases of priority chemicals can be reduced. The best way to reduce the use of priority products, and thus, priority chemicals, is to identify safe substitutes that effectively perform the same function without adverse environmental consequences or human exposure.

Identification of Priority Chemicals

The identification of priority products in this study focused on products that either contain or use compounds included in the U.S. EPA's 33/50 Program. The 33/50 Program is a voluntary pollution prevention initiative intended to achieve reductions in pollution in a relatively short time frame. The program enlisted companies in important industry sectors to make voluntary commitments to reduce reported releases and transfers of 17 priority chemicals. Participating companies were asked to develop their own reduction goals contributing toward national reduction goals of 33 percent by 1992 and 50 percent by 1995. Reductions are measured against a 1989 baseline of information reported to EPA under the Toxic Release Inventory (TRI). EPA is seeking reduction primarily through pollution prevention practices which go beyond regulatory requirements.

The 33/50 chemicals include the following:

- Metals and Metal Compounds
  cadmium
  chromium
  lead
  mercury
  nickel

- Organic Chemicals
  benzene
  toluene
  xylenes
  methyl ethyl ketone
  methyl isobutyl ketone

- Halogenated Organic Chemicals
  carbon tetrachloride
  chloroform
  tetrachloroethylene
  dichloromethane (methylene chloride)
  1,1,1-trichloroethane
  trichloroethylene

- Cyanide Compounds

EPA selected these compounds for the voluntary pollution prevention initiative based on a number of factors, including their high production volume, high releases and off-site transfers of the chemicals relative to their total production, opportunities for pollution prevention, and their potential for causing health and environmental effects.

The Safe Substitutes Project also included a major task to develop a chemical ranking and scoring system for the systematic selection of priority chemicals for substitutes assessments. This ranking and scoring system was developed using available data on human health and environmental toxicity together with data relating to the potential for exposure. An algorithm was developed to combine the various endpoints and

exposure potential into an overall hazard value and ranking for a group of chemicals from the TRI list and for high-volume pesticides. The chemical ranking and scoring system and the results of its application to this list of chemicals is contained in a separate report entitled, *Chemical Hazard Evaluation for Management Strategies: A Method for Ranking and Scoring Chemicals by Potential Human Health and Environmental Impacts.*

Identification of Priority Products

Using the 33/50 chemicals as the priority chemicals for this project, a list of priority products was developed by determining the most important uses of each chemical and the products that either incorporate it into their formulations or rely upon it heavily in the manufacturing process. Priority products for each chemical represent those significant uses that also result in significant environmental releases of the priority chemical.

A useful tool was developed for identifying priority products for each of the priority chemicals: the chemical-use tree diagram. Chemical-use tree diagrams show the step-wise progression of the use of a chemical, from the raw material stage through the final consumer or industrial use of the chemical or use of consumer products manufactured from the chemical. Figure ES.1 is the chemical-use tree diagram developed for cyanides, which is an example of the chemical-use trees that are contained in this report that were developed for each of the priority chemicals. The numbers along the branches of the use tree are weight fractions of the usage of the chemical or product in the first box to produce the chemical or product in the second box. In this particular case, reliable data were not available to quantify the uses along some branches of the use tree, since such data is difficult to obtain from the published literature.
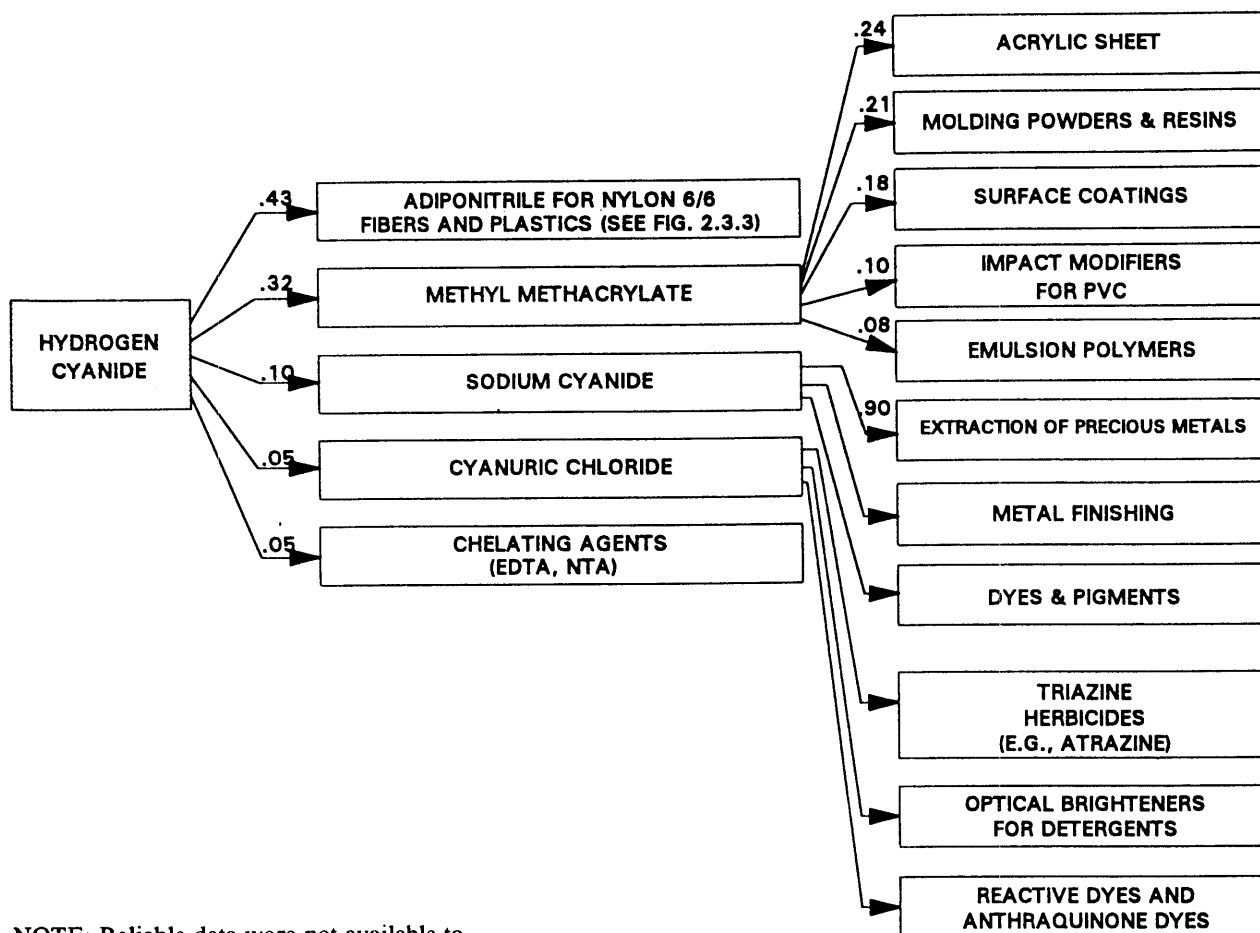
FIGURE ES.1   CYANIDE CHEMICAL-USE TREE

NOTE: Reliable data were not available to estimate weight fractions along some branches of the chemical-use tree.

As the priority products for each of the 33/50 chemicals were identified, it became apparent that some of the priority products clustered into a few overall use clusters involving the use of more than one of the priority chemicals. These included, for example, paints and coatings, which require use of the 33/50 organic chemicals and some of the 33/50 metals and also result in the use of paint strippers utilizing one of the 33/50 halogenated organics. Four of the priority product classes selected for substitutes evaluation represented use clusters involving more than one of the 33/50 chemicals. Figure ES.2 illustrates the use clusters among the priority products chosen for substitutes evaluation, as well as priority products that were selected to represent major uses of single chemicals from the 33/50 list.

Priority products were also identified for which substitutes assessments were not performed. These priority products can be the subject of future research. This report is intended to demonstrate the concept and methodology of chemical use evaluation and substitutes assessment for a limited number of priority products.
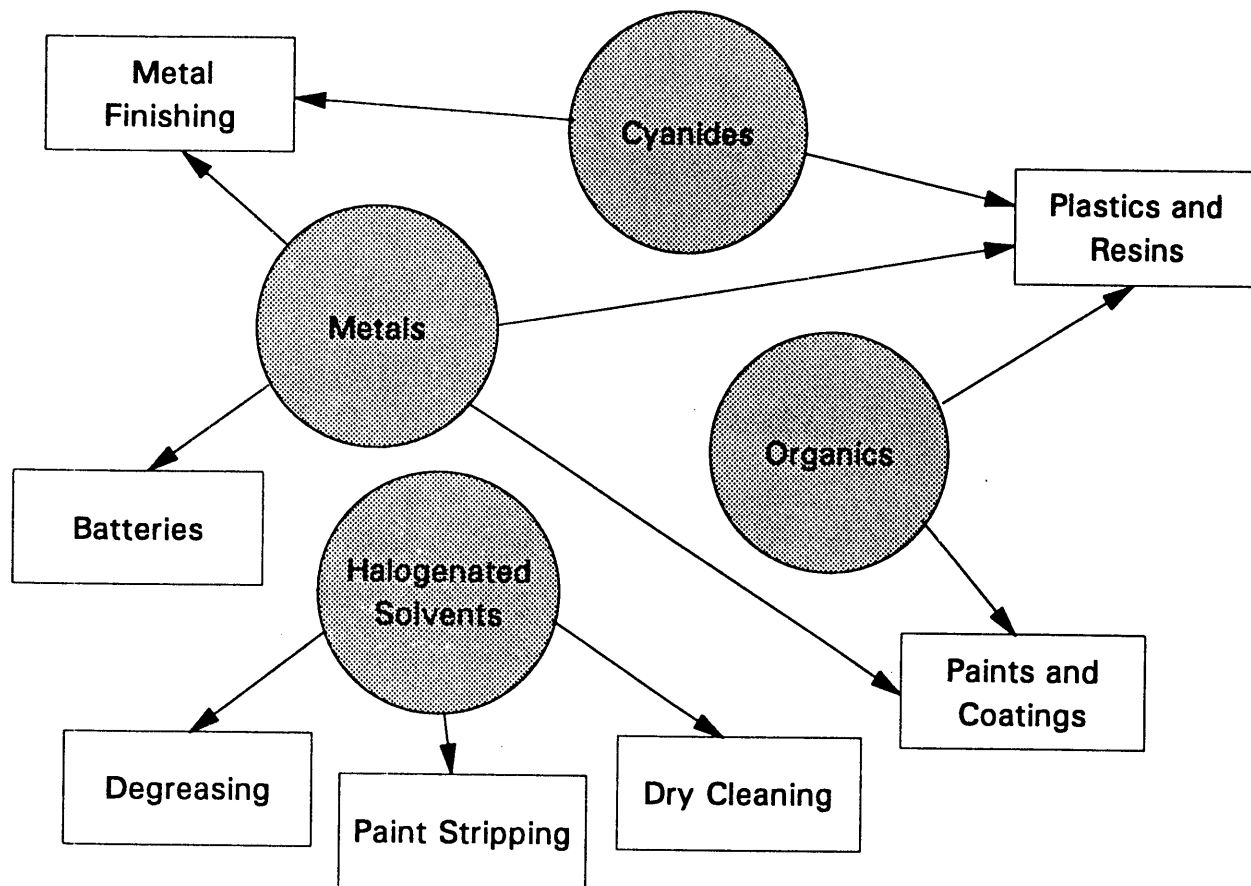
FIGURE ES.2   PRIORITY PRODUCTS OF 33/50 CHEMICALS

There are three ways of reducing toxic chemical releases by focussing on products: redesigning products to reduce or eliminate toxic chemical components; replacing products that contain or rely upon toxic chemicals with different products that do not; and substituting chemicals or redesigning manufacturing processes to reduce or eliminate the use of toxic chemicals to manufacture the products.

Identification and Evaluation of Existing Substitutes for Priority Products

This report contains an identification and preliminary evaluation of existing substitutes for the priority products selected for assessment. There are basically three ways of reducing toxic chemical releases by focussing on products:

■ redesigning products to reduce or eliminate toxic chemical components;

- replacing products that contain or rely upon toxic chemicals with different products that do not; and

- substituting chemicals or redesigning manufacturing processes to reduce or eliminate the use of toxic chemicals used to manufacture the products.

The substitutes assessments were based on literature reviews, vendor contacts, and user contacts and did not include demonstration of the substitutes or verification of their performance through independent testing. The evaluations of the substitutes discuss the degree to which they have been developed, demonstrated, and commercialized.

First, literature was reviewed to determine the specific properties or functions for which each priority product was developed. Where necessary, vendors and users of priority products were contacted to determine particular reasons why each priority product is used. Literature was then reviewed to identify existing substitutes for each priority product and to determine as much as possible about the efficacy of the substitutes, their impact on reducing hazardous waste generation and chemical releases, impediments to substitutions and their economics as compared to the original products. Vendors and users of substitutes were also interviewed to obtain current information on safe substitutes and other information not available in literature. Finally, experts were enlisted in certain product areas to evaluate substitutes.

ORGANIZATION OF THIS REPORT

This report is organized into two parts. Part I contains the discussion of each of the priority chemicals and the selection of priority products for substitutes assessments. It is divided into four chapters for each of the four classes of 33/50 chemicals: organic chemicals; halogenated organic chemicals; metals; and cyanide compounds. For each of the chemicals, the discussion includes the physical properties, health and environmental issues, an industry profile on manufacturers, the supply and demand, the price, the production processes, environmental releases and transfers from the TRI, and an analysis of uses. A chemical-use tree is also presented for each of the chemicals.

Part II of the report contains the discussion of each of the priority product groups or use clusters for which substitutes assessments were performed in this study. This discussion includes an industry profile, the quantity of 33/50 chemicals used in the manufacturing of the product, the important properties of the product which result in the use of 33/50 chemicals, the environmental releases and transfers of 33/50 chemicals during the production of the product, and a focussed discussion of health, safety and environmental issues related to the product.

Part II of the report also contains an evaluation of safe substitutes for each priority product group or use cluster. These substitutes span the gamut from simple product replacements (e.g., use of reusable cups to replace polystyrene disposables); to product redesign (e.g., substitution of biopolymers for polystyrene foam packaging); to substitutions for toxic chemicals in manufacturing processes (e.g., use of aqueous parts cleaning solutions in electronics manufacturing).

RESULTS OF THE RESEARCH

Following is a brief summary of the results of the research.

Priority Chemicals

Metals and Metal Compounds. The 33/50 metals and metal compounds studied in this project included:

cadmium and compounds;
chromium and compounds;
lead and compounds;
mercury and compounds; and
nickel and compounds.

The amounts of these metals consumed in the United States (U.S.) in 1992 is presented in Table ES.1.

TABLE ES.1
33/50 METALS DEMAND IN THE U.S.
IN 1992

Metal	Amount Consumed (1992) (million pounds)
Cadmium	8.20
Chromium	692.60
Lead	2,672.60
Mercury	1.36
Nickel	261.40

These metals are released into the environment during extraction, smelting and refining, use in manufacturing, and in disposal of products containing them. The primary metals industry released more than 43 million pounds of the 33/50 metals and their compounds to the environment in 1991, nearly 42 percent of total releases of these metals and compounds. The chemical and allied products industry contributed about 24 million pounds, about 23 percent of the total releases, most of which were chromium compounds. Other industries that contributed significantly were fabricated metals and the electrical industry.

Table ES.2 shows the total releases and transfers for each of these metals and compounds. Throughout the report the quantities of releases and transfers do not include transfers

to recycling and energy recovery facilities, consistent with EPA's policy on reporting TRI data.

TABLE ES.2
TOTAL RELEASES AND TRANSFERS OF 33/50 METALS AND COMPOUNDS IN 1991

Metals and Compounds	Environmental Releases and Transfers (million pounds)
Cadmium	2.04
Chromium	48.87
Lead	39.75
Mercury	0.22
Nickel	12.94
TOTAL	103.82

Although there are more significant uses of some of the individual metals, major uses of the 33/50 metals throughout industry are found in three broad use clusters: batteries (cadmium, lead, mercury, nickel); electroplating of metals (cadmium, chromium, nickel); and pigments for paints, plastics, and inks (cadmium, chromium, and lead). **Batteries and electroplating were selected for substitutes assessments as the largest overall end-uses of the 33/50 metals.** Cyanides, another class of 33/50 chemicals, are also widely used in electroplating.

Organic Chemicals. The 33/50 organic chemicals studied were:

benzene;
toluene;
xylenes;
methyl ethyl ketone; and
methyl isobutyl ketone.

The amounts of these chemicals produced in the U.S. in 1992 are presented in Table ES.3.

TABLE ES.3
DEMAND FOR THE 33/50 ORGANIC CHEMICALS IN 1992

Chemical	Demand (1992) (million pounds)
Benzene	13,790
Toluene	13,650[a]
Xylenes	14,040[a]
MEK	490
MIBK	175

[a] Capacity data for 1992. Demand data not available.

The first three organic chemicals, benzene, toluene, and xylenes (BTX), are produced primarily from petroleum. Petrochemical feedstock, which is used to produce BTX and other chemicals, comprises only about three percent by volume of the products of crude oil. The two ketones, MEK and MIBK, are produced from sec-butyl alcohol and acetone, respectively.

Environmental releases of the 33/50 organic chemicals occur during the refining of petroleum, in the production of the chemicals themselves, and in their distribution and use in manufacturing chemical intermediates and final products. These chemicals may also be incorporated in products from which they are ultimately released to the environment.

In the TRI, which covers only releases of the chemicals from manufacturing industries, the chemicals and allied products industries reported the greatest amount of releases and transfers of the 33/50 organic chemicals in 1991, 95.5 million pounds or about 18 percent of the total, with toluene and xylene releases predominating.

Transportation, rubber and plastic products, and industries reporting multiple SIC Codes also had a significant percentage of the total releases.

Table ES.4 shows the total releases and transfers of the 33/50 organics.

TABLE ES.4
TOTAL RELEASES AND TRANSFERS OF THE 33/50 ORGANIC CHEMICALS IN 1991

Chemical	Releases and Transfers (million pounds)
Benzene	20.86
Toluene	223.50
Xylenes	146.70
MEK	114.90
MIBK	30.80
TOTAL	536.76

Benzene, toluene, and xylenes are basic building block chemicals that are widely used in the manufacture of many products. The major uses of these compounds cluster in two broad use clusters: plastics and resins precursors (benzene, toluene, xylenes) and paints and coatings solvents (toluene, xylenes, MEK, MIBK). Two other 33/50 chemicals, cyanides and dichloromethane, are also used to manufacture plastics and resins. Metals on the 33/50 list are used as pigments in plastics and in paints, and another 33/50 halogenated organic chemical, dichloromethane, is used in paint stripping. **The substitutes assessments for this class of 33/50 compounds focussed on a particular plastic, polystyrene, and on the use of the chemicals as paints and coatings solvents.**

Halogenated Organic Compounds. The 33/50 halogenated organic compounds studied in this project were:

dichloromethane (methylene chloride);
chloroform;
carbon tetrachloride;
perchloroethylene;
trichloroethylene; and
1,1,1-trichloroethane.

The U.S. demand for these chemicals in 1992 is shown in Table ES.5.

**TABLE ES.5
U.S. DEMAND FOR 33/50 HALOGENATED ORGANIC CHEMICALS IN 1992**

Chemical	U.S. Demand (1992) (million pounds)
Dichloromethane	390
Chloroform	485
Carbon tetrachloride	250
Perchloroethylene	250
Trichloroethylene	145
1,1,1-Trichloroethane	600

The production of these halogenated solvents is very interrelated, and also related to the production of chlorofluorocarbons. Dichloromethane and chloroform are co-products, as are carbon tetrachloride and perchloroethylene by one process, and trichloroethylene and perchloroethylene by another. The ratio of the co-products in each case can be adjusted by the manufacturer depending upon the demand for the ultimate products produced. Chloroform, carbon tetrachloride, and perchloroethylene have each had major usage as intermediates in the production of chlorofluorocarbons.

Environmental releases of the 33/50 halogenated organics occur during the production of the compounds, in their uses in

manufacturing, and in some cases as a result of their presence in consumer products. In the 1991 TRI, the largest source of environmental releases and transfers was the chemicals and allied products industries, with nearly 16 percent of the releases, mostly dichloromethane. The next largest sources were the rubber and plastic products industry (14.5 percent), the transportation industry (12 percent), fabricated metals industry (10 percent), and electrical industry (8 percent), which use halogenated solvents for degreasing. The major source of chloroform releases is the pulp and paper industry, which creates chloroform as a byproduct of the chlorine or hypochlorite bleaching of wood pulp.

The releases from certain uses of the 33/50 halogenated organics are not reported at all in the TRI. These include the releases of perchloroethylene from dry cleaning and the releases of dichloromethane from the use of paint strippers sold as consumer products.

Table ES.6 presents the total environmental releases and transfers of the 33/50 halogenated organics from the 1991 TRI.

**TABLE ES.6
TOTAL RELEASES AND TRANSFERS OF THE 33/50 HALOGENATED ORGANICS IN 1991**

Chemical	Total Releases and Transfers (million pounds)
Dichloromethane	94.8
Chloroform	22.6
Carbon tetrachloride	2.6
Perchloroethylene	20.8
Trichloroethylene	38.0
1,1,1-Trichloroethane	146.0
TOTAL	324.8

The single largest use (approximately 37 percent) of the 33/50 halogenated organic compounds is as a precursor in the manufacturing of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Due to regulatory phase-outs of carbon tetrachloride and CFCs at the end of 1995, this use is declining rapidly for carbon tetrachloride, which is the precursor for CFC-11 and CFC-12, and for perchloroethylene, which is the precursor for CFC-113. The use of chloroform to produce HCFC-22, on the other hand, will continue beyond 1995. EPA proposes phasing-out the HCFCs with the highest depletion potential by 2005, with exceptions made for the servicing of equipment until 2015.

The second largest use of these chemicals (approximately 24 percent) is for materials and parts degreasing in several industries, including the transportation industry, the fabricated metals industry, and the electrical industry. Trichloroethylene, 1,1,1-trichloroethane, and to a lesser extent, dichloromethane and perchloroethylene, have been used for cleaning machined parts and electrical components. Production of 1,1,1-trichloroethane is being phased-out by the end of 1995.

Other major uses include dry cleaning for perchloroethylene, resulting in 50 percent of the demand for this chemical, and paint stripping for dichloromethane, resulting in about 31 percent of the demand for this chemical. Commercial paint strippers sold to consumers and paint strippers used in manufacturing applications both contain dichloromethane.

The uses of 33/50 halogenated organics are found in clusters with other 33/50 chemicals. The use of halogenated organics in parts degreasing is related to the use of toxic metals and cyanides in electroplating and the use of organic solvents in paints and coatings, since machined parts are typically cleaned prior to electroplating or application of coatings. The use of halogenated organics as paint strippers is also related to the use of organic solvents in paints and coatings, since certain coatings applications necessitate the use of paint stripping.

The substitutes assessments in this study focussed on the use of 33/50 halogenated organics in parts degreasing, in dry cleaning of fabrics, and in paint stripping. Although the use as precursors for chlorofluorocarbon production was the greatest use of these compounds, the assessment of substitutes for this use was not performed in this study because the development of substitutes has received a tremendous amount of attention as a result of the phase-outs of CFCs.

Cyanides. The fourth class of 33/50 compounds included in this report is cyanide compounds, including hydrogen cyanide and cyanide salts. The most commonly used cyanide salt is sodium cyanide.

The U.S. production capacity for hydrogen cyanide and sodium cyanide in 1993 and 1991, respectively, is shown in Table ES.7. Hydrogen cyanide production is reported to be near capacity, but sodium cyanide production is estimated to be about 55 to 70 percent of capacity. Hydrogen cyanide is most commonly produced by reaction of methane, ammonia, and air (oxygen). Sodium cyanide is produced by neutralization of hydrogen cyanide with sodium hydroxide.

TABLE ES.7
U.S. PRODUCTION CAPACITY FOR CYANIDES

Chemical	Production Capacity[a] (million pounds)
Hydrogen cyanide Sodium cyanide	1,560 (1993) 500 (1991)

[a] Demand data not available.

Environmental releases of the cyanide compounds occur during the production of the compounds, during their use as intermediates in the manufacturing of chemicals and polymers, and for sodium cyanide, during its uses in metal finishing and in gold and silver mining. In the 1991 TRI, the chemicals and allied products industry contributed nearly 78 percent of the releases of hydrogen cyanide and cyanide compounds, with facilities that produce hydrogen cyanide accounting for 21 percent of the hydrogen cyanide releases from this industry sector. The primary metals industry (9 percent) were also significant contributors of cyanide compound releases.

Table ES.8 presents the environmental releases and transfers from the 1991 TRI for hydrogen cyanide and cyanide compounds.

**TABLE ES.8
ENVIRONMENTAL RELEASES AND
TRANSFERS OF HYDROGEN CYANIDE
AND CYANIDE COMPOUNDS IN 1991**

Chemical	Total Releases and Transfers (million pounds)
Hydrogen cyanide	2.2
Cyanide compounds	5.6
TOTAL	7.8

The major uses of hydrogen cyanide are the manufacture of intermediates used in the production of nylon and acrylic polymers and the manufacture of sodium cyanide. Sodium cyanide is used extensively for the extraction of gold and silver from low grade ores in mining, and for electroplating of gold, silver, copper, zinc, brass, and cadmium.

Some of these major uses of hydrogen cyanide and sodium cyanide are found in use clusters with other 33/50 chemicals. The production of nylon and acrylic polymers is also a major use of benzene, a 33/50 organic compound. Electroplating is an important use cluster for the 33/50 metals (e.g., cadmium), and the use of electroplating often requires parts cleaning with some of the 33/50 halogenated organic compounds (e.g., trichloroethylene, 1,1,1-trichloroethane). **The substitutes assessment for cyanides in this study focussed on the use of sodium cyanide in electroplating.**

SUBSTITUTE ASSESSMENTS FOR PRIORITY PRODUCTS

Batteries

Substantial progress has been made in the design and manufacture of batteries that reduce releases of 33/50 metals, with the exception of lead-acid automotive batteries.

Substantial progress has been made in the design and manufacture of batteries that reduce releases of 33/50 metals. In addition to the development of new types of rechargeable batteries, which reduce overall battery consumption and disposal, successful substitutes have been developed for the mercury and cadmium used in batteries.

Low-Mercury and Mercury-Free Batteries. Low-mercury and mercury-free batteries are now available commercially in advance of regulatory deadlines for reductions of mercury content in zinc-carbon cells and in alkaline batteries. Mercury in button cell batteries is being eliminated with the development of zinc-air cells. In addition to reducing releases of mercury from smelting, refining and battery manufacturing, the development of low-mercury and mercury-free batteries should eliminate batteries as one of the largest sources of mercury in the nation's household wastestream.

Nickel-Metal Hydride and Lithium Batteries. Nickel-metal hydride and lithium batteries have been introduced as alternatives to batteries employing a cadmium electrode. Nickel-metal hydride batteries have demonstrated some performance advantages over nickel-cadmium batteries. Although nickel-metal hydride batteries still contain nickel, a 33/50 metal, rechargeable lithium batteries eliminate its use. The lithium battery will not be without potential health and environmental effects, however, as these batteries contain small amounts of arsenic.

Lead-Acid Batteries. Although lead-acid batteries contribute a significantly greater amount of environmental releases and transfers during their manufacture, use and disposal than other types of batteries, development of safe substitutes for lead-acid batteries has not been as successful. Potentially viable substitutes for lead-acid batteries that are currently being evaluated include nickel-zinc batteries, nickel-iron batteries, and sodium-sulfur batteries. These batteries have performance or cost disadvantages that may prevent their wide use, or they may present other potential health, safety and environmental hazards that outweigh those of lead-acid batteries.

Electroplating

> *Substitutes are available to reduce the use of the toxic 33/50 metals and cyanides in many applications through product redesign to eliminate electroplating, through alternative metal deposition techniques, and through new plating baths.*

The complexity of electroplating operations and the various plating baths used in electroplating make it difficult to identify across-the-board substitutes. Substitutes are available, however, to reduce the use of the 33/50 metals and cyanides in many applications.

Product redesign to eliminate the use of electroplating is possible in many cases and can be the best environmental option, since it eliminates the use of both the metal and the plating bath. The printed wiring board industry, for example, has replaced the cadmium-plated steel chassis with boards made from resinous material to eliminate electroplating. Decorative electroplating is also being replaced in some industries by paints and coatings. Of course, paints and coatings have their 33/50 releases and environmental impacts as well.

Metal deposition methods that do not use a plating bath are also available. These include flame and plasma spraying, mechanical plating, and vacuum metalizing. These methods eliminate the hazardous plating bath, but not the use of the toxic metal. One drawback to the alternative metal deposition methods is that metal overspray from spraying methods or turnings from remachining thick coatings may actually increase the consumption of the toxic metals and increase occupational hazards.

Finally, substitutes for the 33/50 metals and for cyanide in plating baths do exist. Zinc, tin-zinc, tin-cobalt, and other alloys have proven to be effective substitutes for cadmium and chromium in decorative and some functional applications. Trivalent chromium has also been demonstrated to be an effective replacement for more toxic hexavalent chromium in some applications. Several non-cyanide plating baths have been developed, including sulfate baths for gold plating and electroless plating, which eliminates both the cyanide bath and the use of electricity.

Plastics and Resins: Polystyrene Packaging and Disposables

> *Biologically derived polymers, based upon starch or lactic acid, are available for a number of applications as replacements for polystyrene.*

The substitutes assessment for plastics and resins focussed on polystyrene packaging and disposables as one of the largest uses of the benzene produced from petrochemical feedstock. Alternatives not only eliminate the releases of benzene and other toxics from production, but also reduce the burden on land-based disposal facilities. The most obvious substitutes consist of eliminating unnecessary packaging and using reusable products instead of throwaways. Disposable paper products have been substituted for polystyrene in some uses, but paper products have their own set of environmental impacts, including the release of 33/50 chemicals (e.g., chloroform).

Biologically derived polymers, based upon starch or lactic acid, are also available for a number of applications as replacements for polystyrene. Not only do biologically derived polymers reduce the use and releases of 33/50 organic chemicals, they also are readily degradable, if properly managed. A more complete analysis of the impacts of these polymers on sewage treatment plants or compost operations, however, needs to be performed.

Paints and Coatings

> *There has been great progress in the development of paints and coatings that reduce the use of 33/50 organic chemicals, including powder coatings and water dispersible coatings.*

There has been great progress in the development of paints and coatings that reduce the use of 33/50 organic chemicals, such as toluene, xylenes, methyl ethyl ketone, and methyl isobutyl ketone, due to regulatory restrictions on volatile organic compound (VOC) content. Safe substitutes for solvent-borne paints are rapidly taking hold within industry and the trade sales sector. For the industrial sector, powder coatings appear to offer the best environmental alternative in reducing releases of 33/50 chemicals. For home use, water dispersible paints are the best choice, since they have the lowest organic solvent content of the water-borne safe substitutes. A no-VOC paint was recently introduced that sets an unexpected new benchmark for the industry.

The safe substitutes for high-solvents paints are not without releases of 33/50 chemicals. Many of the resins used in these paints (methyl methacrylate, polyurethane, and styrene-butadiene, to name a few) are made from 33/50 chemicals. Since variations of these same resins are also used in high-solvent paints, the substitutes clearly result in reductions in releases.

Further research and development should be encouraged to develop substitutes that, for example, meet appearance requirements of the automobile industry or that meet shelf-life requirements for household paints. Strong interest from industrial paint users and consumers is providing impetus for paint manufacturers to increase their research in these areas.

Materials and Parts Degreasing

> *Substantial progress has been made in the use of safe substitutes for the 33/50 halogenated organic cleaning solvents. The no-clean alternative is the preferable substitute for halogenated organic solvents, with aqueous and semi-aqueous cleaners being used in many applications.*

Substantial progress has been made in the use of safe substitutes for the 33/50 halogenated organic cleaning solvents. Examples of industries that are switching to safer substitutes range from the printed wiring board industry, to the automotive parts industry, to portions of the U.S. Department of Energy Nuclear Weapons Complex.

The no-clean alternative is the preferable substitute for halogenated organic solvents. Eliminating the cleaning process altogether avoids some of the potential environmental drawbacks of the aqueous and semi-aqueous cleaner substitutes, discussed below. Redefining unnecessarily stringent cleanliness specifications, eliminating the step which soils the part, or changing the nature of the soil to eliminate the need for cleaning are possible ways to implement the no-clean alternative.

Aqueous and semi-aqueous cleaners have the broadest range of application as safe substitutes for the 33/50 halogenated organic cleaning solvents, although they have some disadvantages. Some of these substitutes are flammable, corrosive, or have limited or no toxicity data. In addition, switching to aqueous or semi-aqueous cleaners generally requires additional equipment, multiple cleaning and rinsing steps, and drying, depending on the cleaning level currently being attained in solvent-based cleaning processes. Substitutes typically require process and facility testing in order to determine optimum cleaning chemistries and equipment.

Dry Cleaning

There are three basic approaches that can successfully reduce the use of perchloroethylene in dry cleaning of fabrics and garments; reducing the use of water sensitive fabrics; modification of the professional dry cleaning process; and substituting petroleum solvents for perchloroethylene.

There are three basic approaches that can successfully reduce the use of perchloroethylene in dry cleaning of fabrics and garments. The first is reducing the use of water sensitive fabrics and garments that require dry cleaning. Second is the modification of the professional dry

cleaning process to eliminate or reduce the use of organic solvents. One process that is currently being demonstrated with EPA participation is an aqueous cleaning process using soaps made from natural oils, hand spot cleaning to remove oily stains, and steam to remove bacteria and odors. Finally, petroleum solvents can be used as substitutes for perchloroethylene. They currently have approximately 10 to 12 percent of the dry cleaning market, primarily for leather and suede cleaning, but have the major drawback of flammability. In fact, perchloroethylene was originally considered a safe substitute for petroleum solvents used in dry cleaning.

Paint Stripping

Media blasting methods have been developed that are safe, effective substitutes for dichloromethane (methylene chloride) paint stripping in the industrial sector, and less volatile substitute chemicals are available in the consumer sector.

Several media blasting methods have been developed that are safe, effective substitutes for dichloromethane (methylene chloride) paint stripping in the industrial sector. These methods are less viable for the consumer, since they typically require expensive equipment. Of the media blasting methods described in this report, the plastic and starch-based methods appear to be gaining the most widespread acceptance. Still, selecting between the various methods requires an evaluation of their environmental tradeoffs.

Plastic media blasting employs polymers made from synthetic organic chemicals that may cause health and environmental effects during their production, but this method does not generate wastewater contaminated with paint particles during the paint stripping process.

Starch-based media blasting generates wastewater that may be contaminated with toxic metal paint pigments, requiring treatment before release to the environment. More evaluation of the life cycle environmental impacts of these alternatives is necessary.

Substitute chemicals for the dichloromethane-based paint strippers for the consumer market are the most viable alternatives since they do not require costly equipment. A number of chemicals have been used or proposed for use as substitutes, including n-methyl pyrrolidone (NMP), dibasic esters (DBEs), paint thinners, and other solvents (e.g., alkyl acetate, diacetone alcohol, and glycol ethers). These chemical substitutes have generally not proven to be as effective in paint stripping as dichloromethane, especially on aged paint.

The less volatile alternative chemical stripping formulations, such as NMP and DBEs, may offer a health and environmental advantage, at least because there is less potential for exposure via inhalation and less potential for air releases. The toxicity of these substitutes needs to be better defined.

CHAPTER 1

METALS AND METAL COMPOUNDS

Five of the seventeen 33/50 chemicals fall within the chemical class of metals and metal compounds. These are cadmium and cadmium compounds, chromium and chromium compounds, lead and lead compounds, mercury and mercury compounds, and nickel and nickel compounds.

The 33/50 metals are elements that exist naturally in trace amounts. The commercial production (extraction and purification), use, and disposal, however, can cause their elevated, sometimes toxic concentrations in the environment. This chapter presents the physical properties of the 33/50 metals and metal compounds; health, safety, and environmental issues associated with their production and use; market trends related to their consumption; mining, smelting and refining processes; environmental releases from use and production and the distribution of environmental releases by industry group; and products or uses of the 33/50 metals and metal compounds.

PHYSICAL PROPERTIES OF THE 33/50 METALS

Cadmium (Cd) is a soft, silver-white, malleable metal. It dissolves readily in nitric acid but slowly in hydrochloric acid and sulfuric acid. Cadmium is relatively insoluble in all bases and in water. It is highly corrosion resistant and stable in air. Cadmium experiences only a slight loss in luster after an extended period of time in air, but when heated in air, it will turn a yellow to brown color as a thin oxide layer forms. If heated to volatilization, it burns with a red-yellow flame to form the poisonous cadmium oxide.[1]

Chromium (Cr) is a steel-gray to silver-white metal that is similar to platinum in luster. The compounds of chromium display a wide variety of brilliant colors. Chromium is very hard, highly acid-resistant, and is only attacked by hydrochloric, hydrofluoric, or sulfuric acid. It is resistant to corrosion and oxidation.[2]

Lead (Pb) is one of the oldest metals to be used by people and the first metal to be obtained from its ore. It is a bluish-white, malleable metal. A lead carbonate that forms on its surface makes it the most corrosion resistant of the common metals. The properties of lead that have contributed to its wide-spread use include its low melting point, ease of casting, high density, low strength, ease of fabrication, acid resistance, and chemical stability in air, water, and soil.[3]

Mercury (Hg) is a heavy, silver-white metal that is liquid at room temperature. Mercury has several unique physical properties that contribute to its many uses. It has a uniform volume expansion over its entire liquid range and a high surface tension which makes it unable to wet and cling to glass. Mercury also has a tendency to form alloys (amalgams) with almost all other metals. Mercury has low resistance to electrical charge and is thus one of the best electrical conductors among the metals. Mercury is stable at ordinary temperatures and does not react with air, ammonia, carbon dioxide, nitrous oxide, or oxygen.[4]

Nickel (Ni) is a light-grey, tough, ductile metal. It is both corrosion and heat resistant, and readily fabricated by hot and cold working. Nickel is slightly soluble in dilute hydrochloric or sulfuric acid, and soluble in dilute nitric acid and in ammonia.[5]

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

The 33/50 metals and metal compounds have similar health, safety, and environmental issues associated with their use and disposal. Long-term exposure to the metals may cause organ damage or, in some cases, cancer. The metals tend to concentrate in the environment from human activities, and have a tendency to bioaccumulate. Issues associated with the use and production of the 33/50 metals and metal compounds, including the sources of environmental releases that may result in adverse

human health or environmental effects, are discussed briefly below.

All of the 33/50 metals have acute or chronic health effects. Cadmium, hexavalent chromium, lead, and nickel are all classified by EPA as known or suspected carcinogens.

Cadmium

Ingestion or inhalation constitute the two primary routes of exposure to cadmium. Short-term exposure to high levels of cadmium causes nausea, vomiting, abdominal cramps, headaches, shortness of breath, fever and respiratory insufficiency. Vomiting can result from water that has a cadmium concentration as low as 15 parts per million (ppm). Long-term exposure causes emphysema, other chronic obstructive pulmonary diseases, kidney damage, anemia, liver disturbance, and a bone disease called Itai-itai.[6] EPA has classified cadmium as a probable human carcinogen (Class B1) based on inhalation data.[7]

Exposure to cadmium may occur from the smelting and refining of zinc, lead, and copper-bearing ores, the production of batteries, the synthesis and use of cadmium-containing pigments, and from its uses in metal plating and coating, soldering, plastics, ceramic glazes, alloys, and amalgams.[8] The most common routes of exposure are from food and tobacco smoke; tobacco may contain one to two ppm cadmium.[9]

Combustion of coal and other fossil fuels releases cadmium into the atmosphere. Disposal of plastics may also contribute to environmental contamination since cadmium is used in stabilizers and pigments. Cadmium enters surface waters mainly from manufacturing operations that involve either cadmium itself or zinc that contains cadmium as an impurity. Plating operations are major contributors where spent plating solutions or rinse waters containing significant amounts of cadmium are discarded. The production of

refined cadmium metal is also a potential source of cadmium in nearby surface waters.[10]

Chromium

Chromium has oxidation states ranging from -2 to +6, but chromium in chemical compounds most commonly occurs in the trivalent (+3) and hexavalent (+6) oxidation states. Trivalent chromium (Cr(III)), which is also the naturally occurring form, has low toxicity due to poor membrane permeability and noncorrosivity. Hexavalent chromium (Cr(VI)), on the other hand, is highly toxic due to strong oxidation characteristics and ready membrane permeability. Thus, the known harmful effects of chromium are primarily attributed to hexavalent chromium.

Chromium enters the body by ingestion, inhalation, and absorption through the skin. Short-term or acute exposure to chromium may cause irritant effects such as contact dermatitis and allergic effects, or oral burn and severe corneal injury. Dermal absorption results in damage to renal tubules.[11]

Effects of long-term exposure to hexavalent chromium include irritation of the nasal mucous membrane and the formation of ulcers and perforations of the nasal septum. All hexavalent chromium compounds are mutagenic, and some are classified by EPA as human carcinogens (Class A).[12] Chronic exposure to hexavalent chromium has been associated with an increased incidence of lung cancer.[13]

Chromium releases into the atmosphere are largely from the chemical manufacturing industry and combustion of natural gas, oil, and coal in which chromium is present as a trace impurity. Electroplating is a major contributor of chromium releases via wastewater, followed by the leather-tanning and textiles industries. Other sources for chromium emissions include wastewater treatment sludge from the production of chrome oxide green pigments, molybdate orange, zinc yellow, and iron blue pigments. These metal emissions include toxic hexavalent chromium. Improper land disposal of municipal incinerator ash and solid waste

from chemical manufacturers may also cause soil contamination.[14]

Under normal conditions, Cr(III) and chromium(0) are relatively unreactive in the atmosphere. Chromium is associated with particulate matter in the air, and is not expected to exist in gaseous form. Most of the chromium in surface waters is present in particulate form as sediment. Hexavalent chromium is the major stable form of chromium in seawater.[15]

Lead

Routes of lead exposure for humans include ingestion, inhalation, and absorption. Lead poisoning affects the nervous, hematologic, gastrointestinal, and cardiac systems. Chronic exposure in adults may lead to hypertension and secondary cardiac effects. In young children, there may be defects in neurological development, including learning disabilities, lowered IQ, and behavioral abnormalities. High levels of exposure may lead to permanent mental retardation and even death. In gastrointestinal systems, lead poisoning alters central nervous system (CNS) control and causes anorexia, constipation, and diarrhea. Toxic levels of lead in the human body can cause sterility in men, and difficulties with pregnancies in women.[16] Exposure to fumes from lead furnaces and to dust from drossing may cause severe lead poisoning.[17] EPA has listed lead as a probable carcinogen (Class B2), based on positive results in animal studies.[18]

Lead may enter the environment through all phases of its production, use, and disposal. When released to the atmosphere, lead is generally in dust form or adsorbed to particulate matter. Atmospheric lead is subject to gravitational settling and transformation to the oxide and carbonate forms.[19]

If released to soil, lead is generally retained in the upper layer of soil. Leaching is not extensive under normal conditions, though some plants take up lead. Lead may be released to surface water in runoff, wastewater, or through atmospheric fallout. Lead does not

3

bioconcentrate significantly in fish but will bioconcentrate in some shellfish such as mussels.[20]

Mercury

Most of the organic and inorganic compounds of mercury are protoplasmic poisons that can be fatal to humans, animals, and plants. Human exposure to mercury may occur by absorption through the skin, ingestion, and inhalation.

Mercury vapor causes acute damage to the lungs and chronic damage to the CNS. Organic mercury compounds can cause toxic dermatitis and can severely damage the CNS. Acute and chronic mercury poisoning may occur when mercury concentrations reach 0.2 mg/100 ml in blood.[21]

Mercury compounds are mutagenic, teratogenic, and embryotoxic, but EPA finds insufficient evidence of their carcinogenicity to classify them as suspected carcinogens. One gram of mercuric chloride ingested orally is thought to be fatal.[22]

One major source of mercury in the environment is the disposal of industrial mercury waste into water where it settles as sediment. Microorganisms convert elemental mercury into methyl mercury salt and dimethyl mercury, which can escape into the atmosphere. About 50 percent of the volatile form of mercury is elemental mercury vapor with a large portion of the remainder being mercury(II) and methyl mercury. Mercury in the environment may be revolatilized many times, with a residence time in the atmosphere of at least a few days. It can be transported hundreds of miles in its volatile phase. Industries like metal smelters or cement manufacturers may be sources of mercury air pollution due to mercury contamination within their products and fuels. Water pollution may originate in sewage or metal refining operations, but mostly from chloralkali manufacturing plants using mercury-based electrolytic cells. Other sources may be combustion of fuels containing mercury impurities and direct releases of various chemical forms of mercury.[23]

Mercury bioaccumulates and biomagnifies up the food chain. Bioconcentration in aquatic species may be as much as 10,000 times the concentration in water. Fish accumulate mercury to very high levels due to rapid accumulation and slow elimination.[24]

Nickel

Inhalation and ingestion of soluble salts are the primary routes of human exposure to nickel. Early symptoms of nickel fume inhalation include headache, sore throat, hoarseness, dizziness, giddiness, and weakness. Other effects of acute inhalation exposure include tightness in the chest, coughing, dyspnea, retrosternal pain, and shortness of breath. Early symptoms of toxicity after ingestion include nausea, vomiting, and diarrhea. An increased incidence of nasal and lung cancer has been noted in nickel workers. EPA classifies nickel refinery dust as a human carcinogen based on human and animal data.[25] Nickel soluble salts are not classified as to carcinogenicity. Contact dermatitis is also a well recognized allergenic reaction to nickel.[26]

Releases of nickel are mainly from the following: nickel ore processing plants; electroplating; production and use of nickel catalyst; parts fabricating and welding; spraying of nickel containing paints; and manufacturing of nickel-cadmium batteries. Food-processing methods add to the nickel levels in foodstuffs through the leaching and the milling of flour using equipment made of nickel alloys, and through the nickel catalytic hydrogenation of fats and oils.[27]

Nickel exists in the atmosphere as particulate matter. Rain transfers airborne nickel to soils and waters. Soil-borne nickel may enter water by surface percolation into groundwater. Physical and chemical interactions that occur in surface and groundwater systems determine the fate and

transport of nickel in those systems. Nickel does not undergo biological transformation in the aquatic environment.[28]

INDUSTRY PROFILE

Ores containing the 33/50 metals and metal compounds are mined at a number of locations in the United States (U.S.) and abroad. Metals and metal compounds consumed in the U.S. may be refined from their ores in the U.S. or imported following the refining process. No attempt was made in this study to identify the numerous national or international mining companies or metal refineries that produce the 33/50 metals and metal compounds. Market trends in the U.S., consumption, and prices of the 33/50 metals are presented below.

Market Trends

Table 1.1 presents U.S. consumption data for the 33/50 metals for the years 1984 to 1992.

U.S. consumption of cadmium fluctuated somewhat over the years of 1984 through 1992. Cadmium consumption saw a recent high in 1986 of just over 4,830 short tons, and a recent low of approximately 3,425 short tons in 1990. Despite decreases in cadmium use within the pigments, stabilizers, and coatings industries, recent increases in the early 1990s are expected to continue due to the increasing market share captured by nickel-cadmium (NiCd) batteries and cadmium-based solar cells.[29] Recycling of NiCd batteries is expected to increase because of economic and environmental reasons.[30]

Industry demand for chromium also fluctuated considerably over the past nine years. The demand peaked in 1989 at almost 620 short tons, compared to a low in 1983 of only about 320 short tons. Demand in 1990 was approximately 440 short tons. The outlook for chromium consumption is strongly tied to the outlook for stainless steel, since stainless steel is the largest end-use of chromium. Worldwide, growth markets

TABLE 1.1   33/50 METALS CONSUMPTION WITHIN THE U.S.

| Year | 1000 Refined Short Tons Per Year | | | | |
	Lead	Nickel	Cadmium	Mercury	Chromium[b]
1984	1250.1[a]	136.86[b]	4.13[c]	2.07[c]	512
1985	1239.2[a]	119.91[b]	4.10[b]	1.89[b]	508
1986	1249.7[a]	107.06[b]	4.83[b]	1.75[b]	427.1
1987	1325.9[a]	130.54[b]	4.60[b]	1.59[b]	557.8
1988	1323.9	149.1	3.99	1.66[d]	607.0
1989	1483.6	140.3	4.52	1.34[d]	618.1
1990	1405.7	137.3	3.42	0.79[d]	443.4
1991	1373.8	139.9	3.68	0.61[d]	413.5
1992	1336.3	130.7	4.10	0.68[d]	346.3[e]

Sources:
Non-Ferrous Metal Data, American Bureau of Metal Statistics, Inc., 1992 (unless otherwise noted)
[a] *Non-Ferrous Metal Data*, American Bureau of Metal Statistics, Inc., 1988
[b] *Metal Statistics*, 85th ed., American Metal Market, 1993
[c] *Metal Statistics*, 78th ed., American Metal Market, 1986
[d] *Mercury Annual Report*, 1992, U.S. Department of the Interior, Bureau of Mines
[e] *Chromium Annual Report*, 1992, U.S. Department of the Interior, Bureau of Mines

for chromium are structural and utilitarian steels, stainless and heat-resisting steels, and other metals and alloys. The remaining chromium markets are considered mature.[31]

> *Increasingly stringent environmental regulations, and reductions and elimination of mercury in consumer products have caused a considerable decline in mercury consumption in the last ten years. Chromium use has also decreased significantly, but U.S. consumption of the other 33/50 metals has been relatively stable.*

Lead consumption in the U.S. increased from about 1.25 million short tons in 1986 to a high of about 1.48 million short tons in 1989.[32] The average annual growth in demand for the period was about three percent. Lead used in storage batteries, including storage battery oxides, accounted for nearly 1.09 million short tons of lead consumption in 1992. Estimates are that the annual growth in lead demand will probably decline 0.5 percent to 1.0 percent per year in the 1990s because of increased emphasis on recycling, as is observed from the data presented for 1991 and 1992. The use of lead is expected to be reduced in nongrowth markets such as solders, paints and coatings, ceramics, containers or other packaging, and cosmetics.[33]

Increasingly stringent environmental regulations caused a considerable decline in mercury consumption in the 1970s and 1980s. Average U.S. consumption dropped on average 4.1 percent per year between 1980 and 1986 and about 1.4 percent per year in the 1970s. Significant reductions and elimination of mercury in consumer products have continued this decrease in mercury use. Projected trends for the mercury market are toward mercury elimination from many products, increased conservation, and recycling because of environmental considerations.[34]

Between 1986 and 1990, annual consumption of nickel fluctuated between a low of about 107,060 short tons in 1986 and a high of 149,100 short tons in 1988. The reported U.S. consumption of nickel and nickel compounds in 1992 was approximately 130,700 short tons. U.S. and world demand for nickel is driven by the stainless steel industry. The U.S. Bureau of Mines predicts nickel consumption will increase three to four percent annually in the 1990s, based on two long-term trends in the stainless steel industry: 1) greater production of stainless steel; and 2) the use of more nickel in stainless steel products. The amount of nickel used in electroplating declined from about 24,200 short tons in 1989 to 14,377 short tons in 1992.[35]

Price of the 33/50 Metals and Metal Compounds

Table 1.2 presents the price of the 33/50 metals between 1984 and 1992. Prices of nickel and cadmium significantly increased in 1988. The cadmium price increase was attributed to labor disputes at mining facilities, the flourishing nickel-cadmium battery industry, and world demand outstripping production.[36] Nickel prices and consumption rebounded from their lowest levels in more than 50 years because of stainless steel demand.[37] Other metal prices have been steady in past years.

PRODUCTION PROCESSES

Metals are typically concentrated from their ores by mining, smelting, and refining. The processes for producing the 33/50 metals from their ores are discussed briefly below.

Cadmium Production

Cadmium is most often found as a trace element (e.g., sulfide ore, greenockite) in copper, lead, and zinc ores. Since cadmium does not occur in high enough concentrations to

TABLE 1.2   PRICES OF 33/50 METALS

Year	U.S. Dollars Per Pound				
	Lead	Nickel	Cadmium	Mercury	Chromium*
1984	0.27	N/A	1.69[b]	4.17	3.75
1985	0.20	3.20[a]	1.21[b]	4.17	3.75
1986	0.22	3.20[a]	1.25[b]	3.20	3.75
1987	0.36	2.29[a]	1.99[b]	3.80	3.51
1988	0.37	6.31	7.60[c]	4.46	3.40
1989	0.39	6.28	6.28[c]	3.91	3.55
1990	0.47	4.23	3.38[c]	3.45	3.55
1991	0.33	3.87	2.01[c]	1.73	3.75
1992	0.36	3.22	0.91[c]	2.55	3.75

Sources:
Metal Statistics, 85th ed., American Metal Market, 1993 (unless otherwise noted)
[a] *Non-Ferrous Metal Data*, American Bureau of Metal Statistics, Inc., 1989
[b] *Non-Ferrous Metal Data*, American Bureau of Metal Statistics, Inc., 1988
[c] *Non-Ferrous Metal Data*, American Bureau of Metal Statistics, Inc., 1992
* Electrolytic chromium (99.8 percent on a metallic basis)
N/A: Not Available

economically justify mining for cadmium alone, it is co-refined with zinc ores (occasionally with lead and copper ores). Concentrations of cadmium in zinc ores typically range from 0.05 percent to 0.8 percent (averaging 0.2 percent) on a weight basis.[38] Principal deposits are located in Scotland, Czechoslovakia, and the U.S.[39] The most important deposits of zinc ores containing cadmium are stratabound-types in platform carbonates. In these deposits, the ores are found in thin zones of replacement mineralization and are the classic Mississippi Valley type of deposits.[40]

Processing begins by grinding the ore until the sulfide minerals of zinc and cadmium become individual grains. The grains are then concentrated by the froth flotation process. This process uses the addition of certain reagents to modify the surface properties of the sulfide particles so that they preferentially adhere to air bubbles streaming through the flotation cell. The sulfide compounds are skimmed off in the froth for further processing by either the pyrometallurgical or hydrometallurgical processes.[41]

In the pyrometallurgical process the sulfide froth material is roasted and sintered. The zinc remains in the oven as zinc oxide, while much of the cadmium impurities are volatilized and become part of the flue dust. The initial concentration of cadmium in the flue dust is about ten percent, but can vary due to differences in the cadmium concentrations in the ore. The cadmium concentrations within the dust can be increased by using a closely controlled kiln or reverberator furnace. Leaching of this flue dust with an acid solution precipitates the cadmium as cadmium carbonate.

In the hydrometallurgical process the zinc/cadmium froth is leached with sulfuric acid. Further steps, including the addition of zinc dust, reduces the cadmium to form a metallic sludge of high cadmium concentration.[42]

Pure cadmium metal is then obtained from both the cadmium carbonate precipitate and metallic sludge by either a leaching or electrolytic process. The leaching process uses a sulfuric acid electrolytic bath (25 to 30 g/l in

concentration) to dissolve the cadmium carbonate or metallic sludge. The cadmium is then oxidized either by blowing air through the solution or adding manganese dioxide. Cadmium is then precipitated as a pure metal sponge by reduction with zinc dust. In the electrolytic process, once metal impurities are first removed (e.g., copper, thallium, lead), the metallic sludge or cadmium carbonate is dissolved in a sulfuric acid bath (100 g/l in concentration). Within this sulfuric acid electrolytic solution is a lead anode and aluminum sheet cathode. When a current is applied, the cadmium deposits as a pure metal sheet on the cathode.[43]

Chromium Production

Chromite is the only ore that contains chromium in concentrations of industrial importance. The U.S. has no chromium reserves and has limited resources, therefore chromite ore used in the U.S. is currently imported.[44]

Chromite is mined by both surface and underground methods. Concentrates are prepared from fines or crushed lower grade ore. The chromite ore is refined by different processes depending on the industry that will be using the chromium product.

The metallurgical industry converts chromite to chromium metal, chromium alloys, or chromium additives by electrochemical or pyrometallurgical processes. The electrochemical process involves the deposition of chromium metal by electrolysis of a purified chromium alum solution. The solution is prepared by a complex process that begins by dissolving ferrochromium in sulfuric acid. The pyrometallurgical process is an aluminothermic reduction, which reduces pure chromic oxide with finely divided aluminum metal.

The chemical industry treats chromite by a hydrometallurgical process. Roasted ground chromite is mixed with soda ash and lime and then leached with a weak chromate liquor or water. Chromite used in the refractory industry is either purchased to size specifications or is

reduced in size with conventional crushing equipment. The crushed product is screened into various ranges of particle sizes.[45]

Mercury Production

The most important mercury ore is the red sulfide ore, cinnabar (HgS). Cinnabar is mined by both surface and underground methods. After the ore has been broken by conventional drilling and blasting, it is removed and crushed. Sometimes this crushed ore is screened to form a "concentrate" before furnacing.

The mercury ore or mercury concentrate is refined by heat in retorts or furnaces to liberate mercury as vapor. The mercury vapor is cooled in a condensing system to form the liquid metal. This method of primary mercury refining produces prime virgin mercury that is more than 99.7 percent pure and acceptable for most industrial uses. Wastes containing mercury (spent liquid mercury cathodes, mercury fluorescent tubes, electrical switches, thermometer breakage, etc.) can also be recycled to recover the mercury.[46]

Lead Production

Lead exists in a variety of ores, but the most commercially important lead ore is galena (PbS). Lead is produced from its ore by mining, milling, smelting, and refining. Lead is often mined using underground operations.

Once mined, the lead ore is crushed to reduce its size to about one millimeter in diameter. The crushed ore is treated by a froth floatation process to recover the lead sulfide in the froth. Smelting of this froth concentrate is conducted in blast furnaces to oxidize the lead and remove the sulfur as sulfur dioxide. At the refinery stage many of the impurities are removed. Calcium and magnesium are added to remove bismuth; potassium nitrate or caustic are added to remove arsenic, antimony, and any traces of calcium or magnesium left from the bismuth process; and zinc dust is added to remove silver and copper. The added zinc and impurities of zinc are removed by vacuum distillation. The refined lead product is 99.95 to 99.99 percent pure.[47]

Nickel Production

Lateritic and sulfide ores are the naturally occurring rock types which contain nickel sulfide concentrations high enough to economically justify mining. Nickel sulfides usually occur as distinct grains within a rock matrix. Once extracted by open pit or underground mining methods, this granular matrix allows for mechanical upgrading by comminution followed by froth flotation separation. The product from these processes, composing of nickel, iron, and copper sulfides, is mixed with silica flux and enters a reverberatory furnace where the iron component of the ore is converted to iron oxide (discarded as slag). The resulting molten product, upon cooling, forms nickel and copper sulfide crystals of high purity.

Crushing of the cooled product and magnetically separating the metallic fractions produces a nearly pure nickel sulfide product. For high grade ores, a nickel sulfide product stream can also be obtained by magnetic separation directly following the mining/comminution process. The nickel sulfide is then pulverized, smelted to form nickel oxide, and reduced (by electrolytic refining or leaching) to form a metallic nickel product.[48]

The U.S. is a major consumer of nickel and imports almost all of its supply of Ni ore. From 1983 to 1986, the production rate of American mines fell sharply, from 9,600 short tons in 1984 to 1,200 short tons in 1986. For the years 1987 and 1988, a negligible amount of ore was mined in the U.S. The largest exporter of Ni ore to the U.S. is Canada, with 51 percent of the total American imports in 1987.[49]

ENVIRONMENTAL RELEASES OF THE 33/50 METALS AND METAL COMPOUNDS

Environmental releases of the 33/50 metals and metal compounds occur from their production, use, and disposal. This section discusses the releases and transfers from the mining, smelting, and refining processes, as well as the distribution of environmental releases by industry group.

Environmental Releases From Production Facilities

Environmental releases of the 33/50 metals and metal compounds resulting from their production occur from mining through smelting and refining. Releases from the mining industry are not required to be reported to TRI, but may be substantial. Releases and transfers of the 33/50 metals and metal compounds from the primary metals industry, which smelts and refines the ore, are reported in the 1991 TRI and are summarized in Tables 1.3 and 1.4. Table 1.3 presents the data for the primary non-ferrous industry (Standard Industrial Code [SIC] 3339). Table 1.4 presents the releases and transfers of cadmium from the primary zinc industry (SIC 3333). On-site releases to land constitute the vast majority of the reported releases and transfers for the primary non-ferrous and primary zinc industries. No releases of lead or lead compounds were reported for the primary lead industry (SIC 3332).[50]

> *Lead and chromium are the 33/50 metals consumed and released to the environment in the greatest quantities. The primary metals industry was the largest emitter of lead reported in the 1991 TRI; the chemical and allied products industry was the largest emitter of chromium.*

Distribution of Environmental Releases by Industry Group

Chromium, lead, and nickel and their compounds were within the top 45 chemicals for TRI total releases and transfers in 1991. TRI releases and transfers in 1991 of cadmium and cadmium compounds ranked number 80, and of mercury and mercury compounds ranked number 146. Table 1.5 lists the total TRI releases and transfers and relative rank of the 33/50 metal compounds.

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TABLE 1.3 RELEASES AND TRANSFERS OF 33/50 METALS FROM THE PRIMARY NON-FERROUS METALS INDUSTRY (SIC 3339)

Releases and Transfers (lbs/yr)

Chemical	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Cadmium	186	0	0	0	186	0	0	0
Cadmium Compounds	19,210	117	125,051	0	144,378	261	0	261
Chromium	0	0	0	0	0	0	0	0
Chromium Compounds	505	0	0	0	505	0	250	250
Lead	625	5	0	0	630	0	0	0
Lead Compounds	450,872	5,284	7,576,165	0	8,032,321	1,052	229,917	230,969
Mercury	0	0	0	0	0	0	0	0
Mercury Compounds	0	0	0	0	0	0	0	0
Nickel	1,001	0	0	0	1,001	0	750	750
Nickel Compounds	1,482	758	542,550	0	544,790	9	0	9
Total	473,881	6,164	8,243,766	0	8,723,811	1,322	230,917	232,239

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

TABLE 1.4   RELEASES AND TRANSFERS OF CADMIUM FROM THE PRIMARY ZINC INDUSTRY (SIC 3333)

Chemical	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Cadmium	0	0	0	0	0	0	0	0
Cadmium Compounds	3,613	1,700	12,181	0	17,494	250	12,168	0
TOTAL	3,613	1,700	12,181	0	17,494	250	12,168	0

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

TABLE 1.5   TOTAL RELEASES AND TRANSFERS OF 33/50 METALS AND METAL COMPOUNDS

Chemical	Releases & Transfers (lbs/yr)	TRI Rank (combined metal and compounds)
Cadmium	1,007,157	80
Cadmium Compounds	1,039,826	
Chromium	8,713,880	21
Chromium Compounds	40,163,165	
Lead	11,337,457	24
Lead Compounds	28,413,286	
Mercury	180,816	146
Mercury Compounds	38,958	
Nickel	5,988,929	45
Nickel Compounds	6,952,629	
TOTAL	103,836,103	

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

Five industry groups accounted for about 83 percent of the environmental releases and transfers of 33/50 metals and metal compounds reported in the 1991 TRI. These industries and their reported releases are presented in Table 1.6. These data do not include the environmental releases from disposal of consumer products that contain these compounds.

The primary metals industry was the largest contributor to releases and transfers of 33/50 metals and metal compounds in 1991, releasing a reported 43 million-plus pounds (almost 42 percent of the total) to the environment. Using the principles of life cycle assessment, these releases can be associated with the final end uses of these metals. Releases from the chemical and allied products industry also constituted a large fraction (23 percent). These releases consisted primarily of chromium compounds.

TABLE 1.6   TOP INDUSTRIES FOR TOTAL TRI RELEASES AND TRANSFERS OF 33/50
METALS AND METAL COMPOUNDS

	Releases and Transfers (lbs/yr)				
Chemical	Chemicals SIC 28	Electrical SIC 36	Primary Metals SIC 33	Fabricated Metals SIC 34	Multiple Code SIC 20-39
Cadmium	1,923	8,119	26,054	595,223	347,003
Cadmium Compounds	138,734	161,724	353,288	218,190	19,106
Chromium	91,261	41,030	3,343,326	1,769,291	176,964
Chromium Compounds	20,968,701	1,128,619	9,612,072	1,299,432	143,602
Lead	14,067	825,454	7,069,553	633,339	1,061,298
Lead Compounds	1,027,493	3,,060,711	18,691,522	650,668	55,981
Mercury	108,773	7,799	265	15	5
Mercury Compounds	36,588	702	270	0	0
Nickel	166,448	99,960	1,642,671	1,294,647	442,431
Nickel Compounds	1,458,472	485,088	2,396,671	689,147	21,020
TOTAL RELEASES AND TRANSFERS	24,012,460	5,819,206	43,135,692	7,149,952	6,539,718
PERCENT OF TOTAL RELEASES AND TRANSFERS	23.13	5.60	41.54	6.89	6.30

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

USES OF THE 33/50 METALS AND METAL COMPOUNDS

The 33/50 metals and metal compounds are widely used in metal finishing processes, in consumer products like batteries and electronic components, in alloys, and in chemical manufacturing processes. The uses of the 33/50 metals are illustrated in chemical-use tree diagrams shown on Figures 1.1 through 1.5. Figure 1.1 presents the uses of cadmium.[51] Figure 1.2 presents the uses of chromium.[52] Figure 1.3 presents the uses of lead.[53] Figure 1.4 presents the uses of mercury[54]. Figure 1.5 presents the uses of nickel.[55]

The numbers along each branch of the chemical-use tree are weight fractions of the usage of the intermediate or product in the first box to produce the intermediate or product in the second box. For example, in Figure 1.2, 18 percent of the chromium produced is used to manufacture chemicals; 90 percent of the chromium chemical products are sodium bichromate; 55 percent of the sodium bichromate is used to manufacture chromic acid. Chromic acid is used to produce wood preservatives, in metal finishing, and other applications.

Closer inspection of the chemical-use trees reveals that many of the 33/50 metals are used to provide similar functions, i.e., use clusters. For example, pigments/oxides are a final product of the metals chromium, cadmium, and lead, while metal finishing (and electroplating) utilizes the metals chromium, cadmium, and nickel as products or process materials. Further evaluation of these product relationships between the 33/50 metals were used to identify use clusters that utilize the greatest fraction and/or greatest number of metals in the broadest applications. Three broad application use clusters were identified: batteries, electroplating (metal finishing), and pigments. Batteries and electroplating, as the two largest overall end-uses of the 33/50 metals, were selected for substitutes assessment.

Battery Manufacture

Cadmium, lead, mercury, and nickel are all used to manufacture batteries. The metal or metal compound typically serves as the cathode or anode material, although mercury is also used to improve the efficacy of some batteries by coating the metal electrode to limit the potential for hydrogen gas evolution.

Batteries have been identified as one of the largest sources of concentrated metals in the environment, since they are frequently discarded by the consumer when they are depleted.[56] A recent study of municipal solid waste in Vancouver, Canada, however, did not identify lead-acid batteries as one of the largest sources of lead in the waste samples analyzed.[57] Recent efforts to recycle batteries and produce rechargeable batteries show promise as a means of reducing the potential environmental impact of batteries, but do not provide a complete solution. While it is recognized that batteries are an integral part of many technologies and products, efforts are underway to develop batteries made from less toxic materials. The evaluation of safe substitutes in Chapter 5 focuses on battery substitutes of this type.

> *Evolution of the chemical-use tree diagrams reveals many products and processes that use more than one 33/50 metal or metal compound. Two use clusters, batteries and electroplating, were selected for substitutes analysis.*

Metal Finishing

Metal finishing includes electroplating and other processes to increase the corrosion resistance, hardness, aesthetic value, or other properties of a product. Cadmium, chromium, and nickel are all widely used to electroplate metal substrates. Electroplating was selected for substitute evaluation because of its broad-range use, because substantial releases to the environment occur from electroplating (from both the manufacturing and the disposal of products), and because a substantial reduction of

electroplating with the 33/50 metals could significantly lower the total environmental releases and hazardous waste disposal of these metals. Cyanides, another class of 33/50 chemicals (discussed in Chapter 4), are also used in electroplating.

Frequently, electroplating is only performed for decorative purposes, although it is more commonly used to improve the corrosion-resistance and increase the hardness of the substrate. Metal finishing technologies are available that use less toxic chemicals and, in some cases, less toxic and more environmentally benign coating technologies may be substituted for electroplating. Safe-substitutes for 33/50 metals and cyanides in electroplating applications are discussed in Chapter 6.

Pigments

Inorganic pigments provide color, opacity, hiding power, and other properties to paints and coatings, plastics, and inks. Many of these products are ultimately released to the environment through paint stripping or disposal of household products such as plastic containers. In addition, exposure to inorganic pigments in household paints is not uncommon, as evidenced by numerous studies of lead poisoning in children.

Lead pigments are still used in some applications, although their use was dramatically curtailed when the effects of lead exposure from paints were well documented. Cadmium and chromium pigments still see wide-spread use.
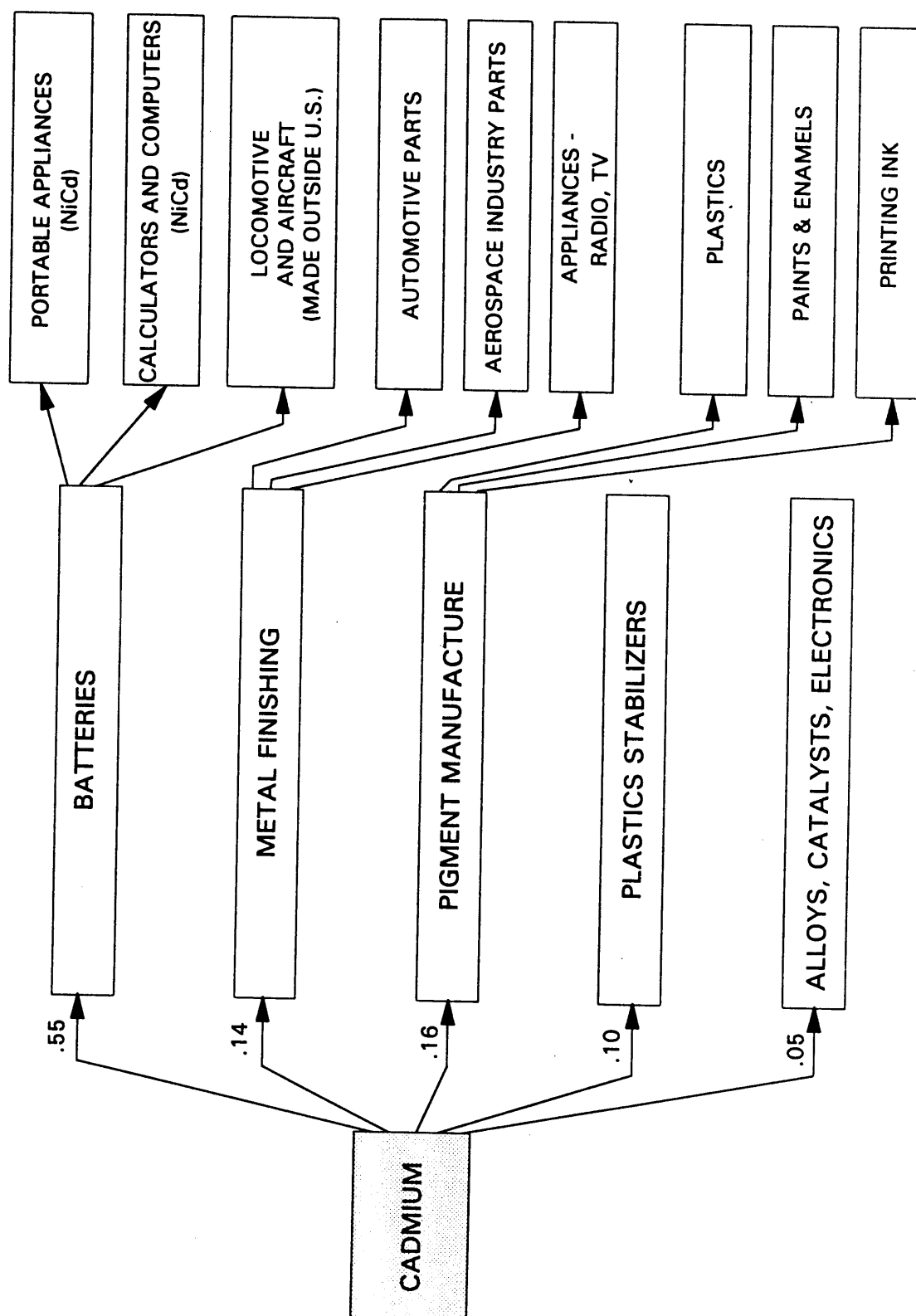
FIGURE 1.1   CADMIUM

Note: Reliable data were not available to estimate weight fractions along some branches of the chemical-use tree.

16

FIGURE 1.2   CHROMIUM

17
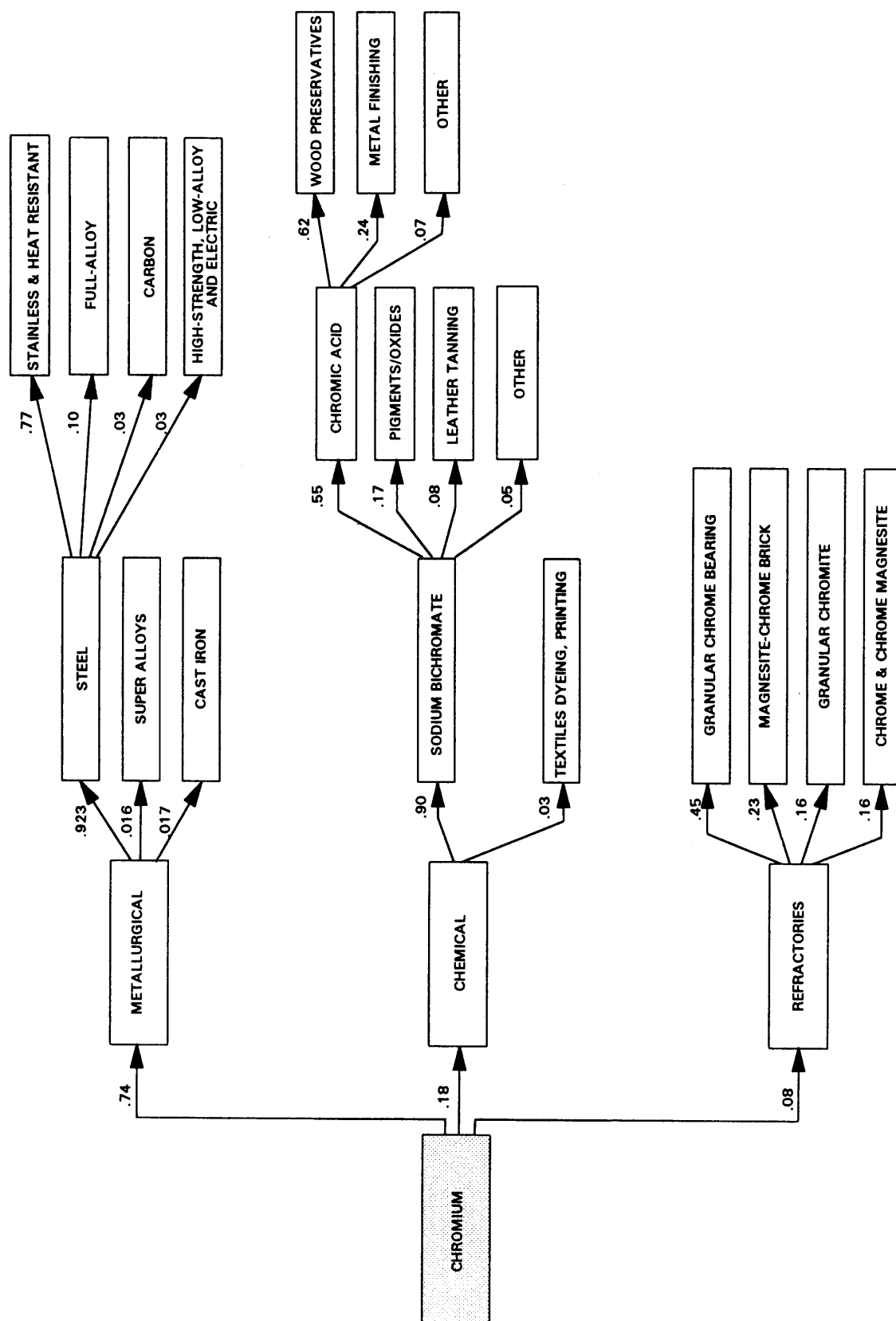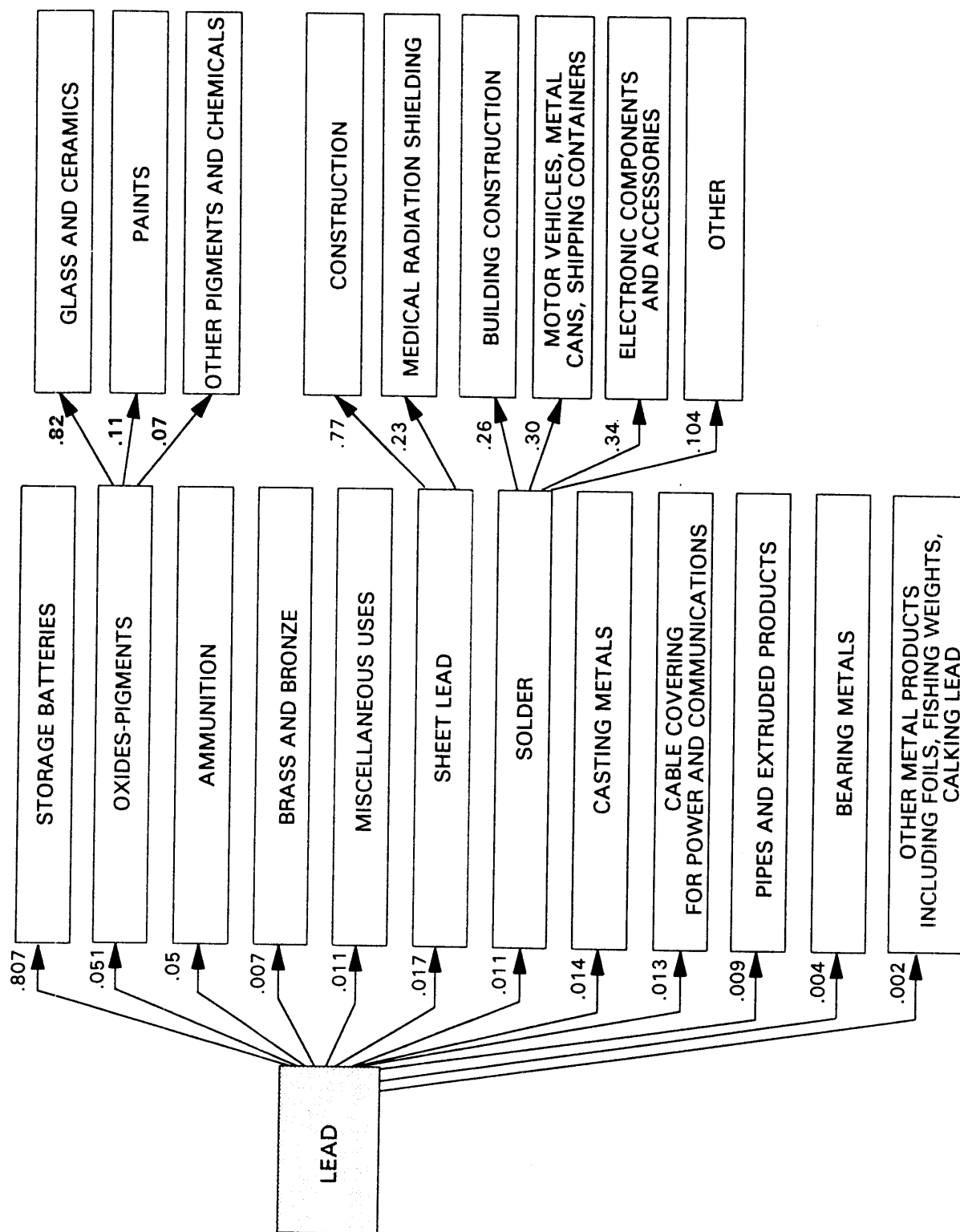
FIGURE 1.3   LEAD
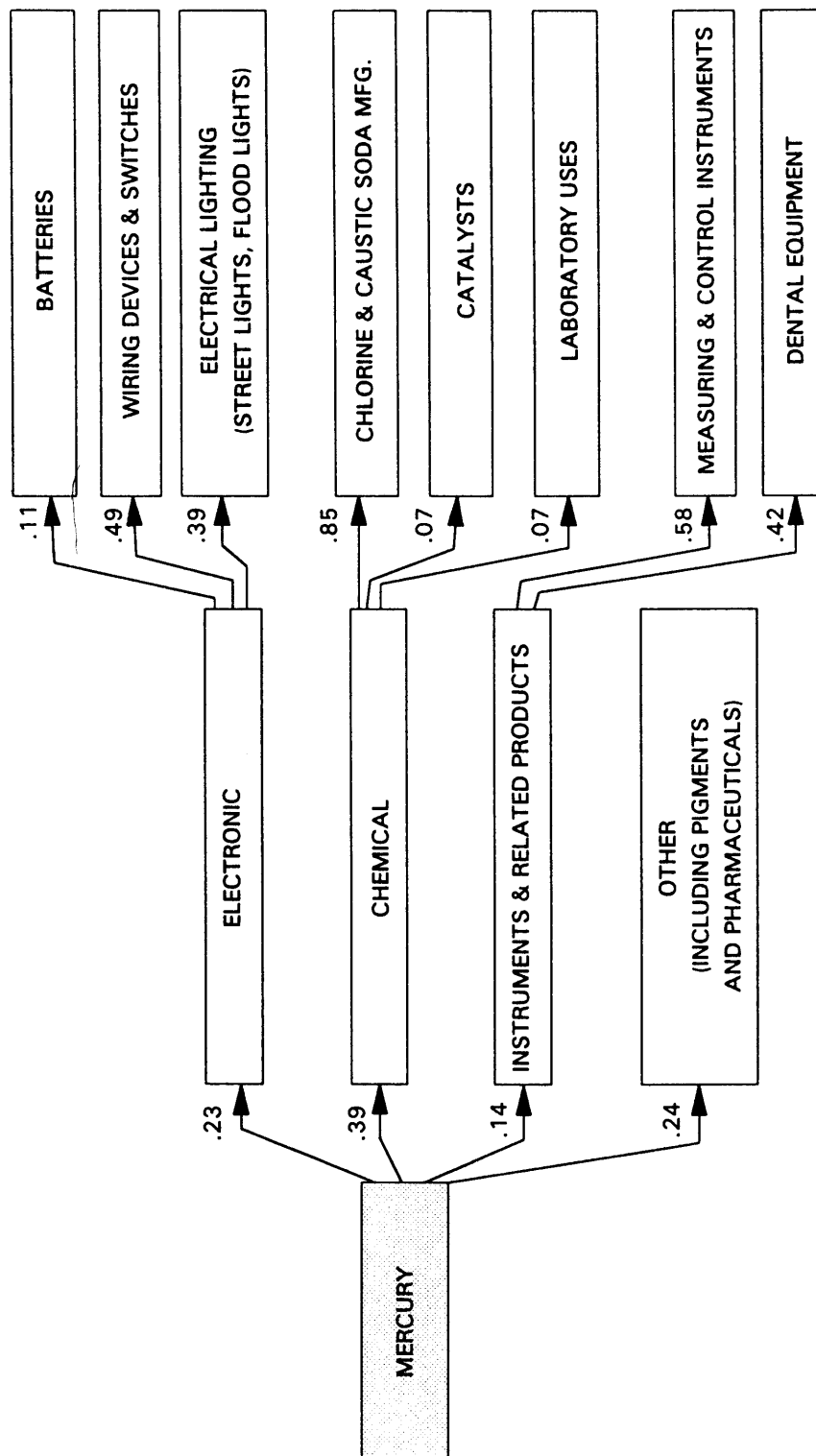
FIGURE 1.4   MERCURY
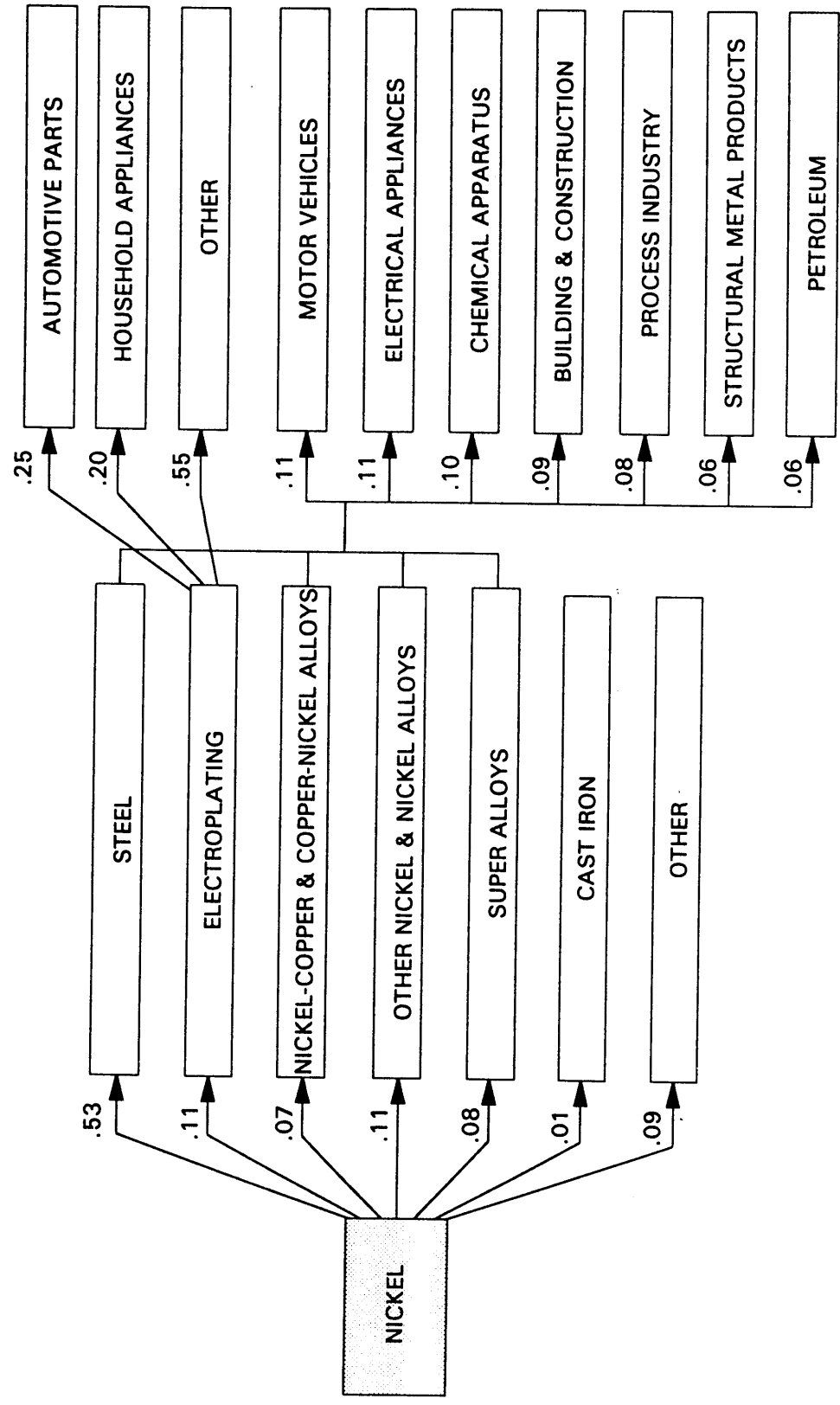
FIGURE 1.5 NICKEL

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CHAPTER 2

ORGANIC CHEMICALS

The 33/50 class of organic chemicals includes benzene, toluene, mixed or unmixed isomers of xylenes, methyl ethyl ketone (MEK), and methyl isobutyl ketone (MIBK). Benzene, toluene, and xylene (BTX) are members of the chemical group known as aromatics. MEK and MIBK are ketones. The 33/50 aromatic compounds are naturally occurring components of crude oil and coal tar. MIBK occurs naturally in some foods; MEK is a synthetic compound not found in nature.

PHYSICAL PROPERTIES

Selected physical properties and the chemical formulae of BTX and the 33/50 ketones are shown in Tables 2.1 and 2.2, respectively. The physical characteristics of these chemicals are discussed briefly below.

Aromatic Compounds

Benzene is the basic unit of the aromatic class of compounds and the source of a wide variety of synthetic organic chemicals. It is a clear, colorless, volatile, and flammable liquid that has a high-octane rating and is thus an important component of gasolines. Benzene is an excellent solvent, but its use as a solvent has been almost eliminated because of its high toxicity.[1] Benzene is thermally stable to oxidation, but may be oxidized to water and carbon dioxide under severe conditions.[2] Benzene primarily reacts with other compounds by substitution and addition.

Toluene is a clear, sweet-smelling, colorless, and noncorrosive liquid. It is a flammable and combustible material that may be ignited by heat, sparks, or flames. After World War II, petroleum displaced coal tar as the main source of toluene. Like benzene, toluene has a high octane rating and therefore is an important compound of gasoline.[3]

The xylene isomers are clear, colorless, volatile, and flammable liquids that have a characteristic sweet odor and a high octane rating.[4] The technical grade of xylene is a mixture of ethylbenzene and the three xylene isomers: o-xylene, m-xylene, and p-xylene. Because of their similar structures, these three isomers and ethylbenzene exhibit similar properties, but their different boiling and freezing points allow them to be separated. A typical mixed xylene contains 20 percent o-xylene, 45 percent m-xylene, 20 percent p-xylene, and 15 percent impurities.[5] The chemical reactions of xylenes include isomerization, disproportionation, and dealkylation.[6]

TABLE 2.1 SELECTED PHYSICAL PROPERTIES OF BENZENE, TOLUENE, AND XYLENE ISOMERS

Property	Benzene	Toluene	o-Xylene	p-Xylene	Mixed-Xylene[a]
Chemical Formula	C_6H_6	C_7H_8	C_8H_{10}	C_8H_{10}	C_8H_{10}
CAS No.	71-43-2	108-88-3	95-47-6	106-42-3	1330-20-7
Molecular Weight	78.110	92.140	106.167	106.167	106.167
Boiling Point, at 101.3 kPa, °C	80.1	110.6	144.4	138.4	138.4
Freezing Point, °C	+5.533	-94.960	-25.180	+13.260	+13.260
Specific Gravity, at 20°C	0.8700	0.8667	0.8802	0.8610	0.8610
Viscosity, at 20°C, cP	0.6468	0.5700	0.7500	0.6000	0.6000
Heat of Vaporization, kJ/Kg	433.6[b]	412.3[c]	408.9[c]	395.9[c]	395.9
Heat of Capacity, at 25°C, kJ/kgK	1.708	1.970	1.771	1.711	1.711
Heat of Combustion, MJ/kg	41.84	42.44	43.05	42.95	42.95
Vapor Pressure, kPa at 0°C	3.4660	0.9100	0.1670	0.2317	0.2317
at 20°C	9.970	2.9200	0.6507	0.8685	0.8685
at 30°C			1.181	1.551	1.551
at 40°C	24.190	7.9100	2.046	2.646	2.646
Solubility in Water, at 20°C, g/kg	1.13	0.50[d]	Insoluble	Insoluble	Insoluble
Flash Point, °C	-11.100	+4.444	+32.220	+27.220	+27.220
Critical Temperature, °C	289.40	318.60	357.15	343.05	343.05
Critical Pressure, MPa	4.924	4.109	3.730	3.511	3.511
Critical Density, kg/m³	300.0	291.6	287.7	280.3	280.3

Sources:
Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed., 1978
Solvent Databank (Publication), Texaco Chemical Company
Perry's *Chemical Engineers Handbook*
Ullmann's Encyclopedia of Industrial Chemistry, 5th ed.
[a] 50 to 60 percent p-Xylene
[b] At 80.10°C
[c] At 25°C
[d] At 16°C

TABLE 2.2   SELECTED PHYSICAL PROPERTIES OF 33/50 KETONES

Property	MEK	MIBK
Chemical Formula	C_4H_8O	$C_6H_{12}O$
CAS No.	78-93-3	108-10-1
Molecular Weight	72.10	100.16
Boiling Point, at 101.3 kPa, °C	79.6	114.0
Freezing Point, °C	-86.4	-84
Specific Gravity, at 20°C	0.806	0.802
Viscosity, at 20°C, cP	0.41	0.61
Heat of Vaporization, at 101.3 kPa, kJ/mol	32.8	35.6
Heat of Capacity, at 25°C, kJ/kgK	2.048	1.920
Heat of Combustion, MJ/kg	0.0338	0.0307
Vapor Pressure, at 20°C, kPa	N/A	2.0
Solubility in Water, at 20°C, g/kg	26.8	1.9
Flash Point, °C	-3.9	20
Critical Temperature, °C	260	298
Critical Pressure, MPa	4.4	3.3

Source:
Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 13, 1978
N/A: Not Available

Ketones

MEK, also known as 2-butanone, is a stable, colorless, and flammable liquid with an acetone-like odor.[7] It is relatively soluble in water and miscible with most organic solvents. MEK has excellent solvency for many natural or synthetic resins and gums. MEK is generally considered equivalent to acetone in solvency, but has the advantages of being less soluble in water and having a higher boiling point and lower vapor pressure than acetone.

MIBK, also known as 4-methyl-2-pentanone, is a widely-used aliphatic ketone solvent. It is a colorless, stable liquid classified as a medium boiler. MIBK is miscible with most organic solvents and with mineral and vegetable oils.

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

The 33/50 organic chemicals each have health, safety, and environmental issues associated with their production, use, and disposal. The following sections summarize these issues for the aromatic compounds and the ketones, respectively.

Aromatic Compounds

Benzene. Benzene is a toxic compound with both acute and chronic effects. Benzene may enter the body through inhalation or ingestion, or by rapid absorption through the skin. The symptoms for short-term exposure to benzene include headaches, nausea, euphoria, confusion, loss of muscular control, and irritation of the respiratory and gastrointestinal tract. At greater concentrations, benzene exposure may cause unconsciousness and even death. Long-term benzene exposure can cause injury to the nervous system and bone marrow. The major effect of chronic toxicity is aplastic anemia. Brain damage has been found in postmortem studies of victims of acute and fatal benzene poisoning. Epidemiologic evidence indicates that benzene causes leukemia.[8] The EPA has classified benzene as a human carcinogen (weight-of-evidence Class A).[9]

> *The 33/50 organic chemicals each have health, safety, and environmental issues associated with their production, use, and disposal. Benzene, considered the most toxic of the 33/50 organic chemicals, is a human carcinogen.*

The legal airborne permissible exposure limit (PEL) for benzene, as established by Occupational Safety and Health Administration (OSHA), is 1 ppm averaged over an eight-hour workshift. Benzene is also highly toxic to animals and plants, especially aquatic life. Benzene, however, does not persist in the environment except in groundwater. Benzene is highly mobile in soil and migrates rapidly to groundwater when released to soil.

Sources of benzene in the environment include chemical plants, petroleum refineries, and combustion of fossil fuels. Human exposure to benzene occurs in ambient air, particularly in areas of heavy traffic, near production plants, and around gasoline stations.[10]

Toluene. The toxic effects of toluene primarily affects the CNS. Human exposure to toluene can occur through inhalation and ingestion. Toluene vapors irritate eyes and respiratory tract and may cause dizziness, anesthesia, and confusion. High levels of exposure cause incoordination, ataxia, unconsciousness, respiratory arrest, and death. If ingested, toluene causes vomiting, diarrhea, depressed respiration, and possibly liver and kidney damage. Effects on liver, renal, and nervous systems may be reversible.[11] Toluene is not classifiable as to human carcinogenicity. There are no human data and inadequate animal data for classification (weight-of-evidence Class D).[12] Inhalation of glues, paints, or solvents containing toluene may result in bronchial and laryngeal irritation and respiratory failure. Muscular weakness syndromes and other CNS system damage are also common in toluene sniffers.

Toluene enters the environment from evaporating petroleum fuel, toluene-based solvents and thinners; spills and leaks during transportation, storage, and disposal of fuels and oils; releases from petroleum during its production and as a by-product from styrene production. Automobile emissions are also a large source of toluene releases to the atmosphere. When released on land, toluene is lost by evaporation and microbial degradation. Toluene decomposes quickly in soil and readily evaporates from water. However, since toluene is relatively mobile in soil, it leaches into the groundwater where biodegradation will not occur. When released into surface water, toluene volatilizes to the atmosphere or biodegrades. In the atmosphere, toluene degrades moderately rapidly by its reaction with photochemically-produced hydroxyl radicals. Toluene's half-life in the atmosphere ranges from three hours to one day.[13]

Xylenes. Acute human exposure to xylenes may cause irritation of the skin, nose, and throat, as well as headache, nausea, fatigue, irritability, loss of appetite, reduced coordination, and unconsciousness.[14] Respiratory failure may

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also occur.[15] Reported long-term health effects of xylene exposure include infertility of female workers, disorders during pregnancy, and signs and symptoms of neurological changes. Xylene was not shown to be mutagenic in short-term tests.[16] Xylenes are also EPA Class D, not classifiable as to human carcinogenicity.[17] Xylenes in liquid form are highly toxic to aquatic life.

Xylene isomers are released into the environment from fugitive emissions and automobile exhaust. Industrial sources include emissions from petroleum refining, coal tar and coal gas distillation, and from their uses as solvents for paints and coatings. In addition, evaporative losses during transport and storage of gasoline and emissions from production of other chemicals (e.g., p-xylene for dimethyl terephthalate and terephthalic acid production) also contribute to environmental pollution.

When spilled on land, the xylene isomers will volatilize or be absorbed into the ground. They may degrade during their passage through the soil, depending on their concentration, residence time in the soil, nature of the soil, and the acclimation of the microbial populations. However, once xylene reaches the groundwater, it does not degrade; therefore, xylene is a common groundwater contaminant. Xylene in surface waters is lost to the atmosphere by evaporation. Xylene is not expected to bioconcentrate.[18] In the atmosphere, xylene reacts with hydroxyl radicals and photochemically degrades. The half-life for o-xylene ranges from 1.5 hours in summer to 15 hours in winter, whereas the atmospheric half-life of p-xylene is 1.7 hours in summer and 18 hours in winter. Despite their rapid degradation, xylenes are still commonly detected in ambient air due to the large quantity of xylene emissions.[19]

Ketones

Exposure to the 33/50 ketones may occur through ingestion, inhalation, and skin absorption. Short-term exposure to MEK or MIBK can cause nose and throat irritation, nausea, vomiting, headaches, dizziness, and loss of coordination or balance. Exposure to MEK may also cause numbness in the fingers and arms, numbness and weakness in the legs, and unconsciousness. MIBK also causes loss of appetite, diarrhea, and drowsiness. Repeated or long-term exposure to MIBK can also cause weakness, eye irritation, stomach pain, sore throat, fatigue, insomnia, intestinal pain, enlarged liver, and colitis.[20] EPA has assigned MEK to weight-of-evidence carcinogenicity Class D, not classifiable as to human carcinogenicity; MIBK has not been assigned a weight-of-evidence carcinogenicity classification by EPA.[21]

The relatively high solubility of MEK in water causes it to volatilize slowly. MEK is mobile in soil. It is moderately toxic to aquatic life and contributes to smog formation. MEK does not cause any cumulative toxic effects to animal life. MIBK is slightly toxic to aquatic life and is thought to contribute to smog formation.[22] MIBK has not been proven to cause any cumulative toxic effects.

INDUSTRY PROFILE

One or more of the BTX compounds are produced by at least 26 companies at 43 locations in the U.S. and its territories. Table 2.3 identifies producers of BTX, their production capacities, the raw materials they employ in the manufacturing process, and the projected demand for these compounds.

MEK is produced for sale and distribution by three companies at three locations; MIBK is also produced for sale and distribution by three companies at three locations. None of the major suppliers of MEK and MIBK produce both compounds. Table 2.4 identifies the producers of MEK and MIBK, the production processes they use, their capacities, and the projected demand for these chemicals.

BTX Market Trends

The total production capacity of benzene in 1990 was 17.3 billion pounds; the 1990 consumption or demand for benzene was 13.5

TABLE 2.3   SUPPLY AND DEMAND OF BTX COMPOUNDS

Producer	1992 Capacity (million lbs/yr)					
	Benzene	Toluene	o-Xylene	p-Xylene	Mixed Xylenes	Raw Material and Remarks*
Amerada Hess Corp. St. Croix, Virgin Islands	559	672			1070	CR and T:NC
Amoco Corp. Texas City, TX Decatur, AL Whitting, IN	798	1771		1479 1084	1429 1400	CR:PC and PYG:PC
AroChem International,Inc. Penuelas, Puerto Rico	580	398	198		941	CR and T
Ashland Oil, Inc. Cattlesburg, KY	544	260			180	COLO:FC and CR and T:FC
BP America, Inc. Alliance, LA Lima, OH	472 834	470 723			431	CR:NC and T CR:NC and T
Chevron Corp. Philadelphia, PA Port Arthur, TX Pascagoula, MS	276 943	181 311		510	553	CR:FC and T:FC CR:PC and PYG:PG and T:PC
CITGO Corp. Lake Charles, LA Corpus Christi, TX	421 566	159 398			237	CR CR and T:FC
The Coastal Corp. Westville, NJ Corpus Christi, TX	109 595	159			503	CR T:FC and CR
Dow Chemical U.S.A. Freeport, TX Plaquemime, LA	363 1451	29 72				PYG:FC and T:FC PYG:FC and T:FC
Exxon Corp. Baton Rouge, LA Baytown, TX	834 1067	1330	286	977	1723	CR and PYG:NC CR:NC and PYG and XIS
FINA Port Arthur, TX	464	1055		.	682	CR:PC and T:PC and T:FC
Huntsman Chemical Corp., Bayport, TX	109					T:FC
Kerr-McGee Corp. Corpus Christi, TX	123	296			215	CR:NC
Koch Industries, Inc. Corpus Christi, TX	617	730	176	855	1249	CR:FC and T:FC and XIS
Lyondell Co. Channelview, TX Houston, TX	871 435	333 217	242	424	747	PYG:FC and CR:NC T:NC

| Producer | 1992 Capacity (million lbs/yr) | | | | | |
	Benzene	Toluene	o-Xylene	p-Xylene	Mixed Xylenes	Raw Material and Remarks*
Mobil Corp. Beaumont, TX Chalmette, LA	726 145	361 275	161	165	359	CR:NC and PYG CR:NC
Occidental Corp. Chocolate Bayou, TX Corpus Christi, TX	726 580	181 145			144	PYG and T PYG and T
Phillips Co. Sweeney, TX Guayama, Puerto Rico	80 600	210 535	132	560	266 725	CR and FC CR:FC and T:FC
Salomon, Inc. Houston, TX	36	101			79	CR:NC
Shell Oil Co. Deer Park, TX Wood River, IL	1125 363	217			395	CR:PC and PYG:PC CR:NC
Sun Co., Inc. Marcus Hook, PA Toledo, OH Tulsa, OK	276 145 210	347 463 152			187 373	CR:NC and T:NC
Texaco, Inc. Delaware City, DE El Dorado, KS Port Arthur, TX	109 109 479	296 80 448				CR:FC
The UNO-VEN Co. Lemont, IL	138	137			72	CR and COLO:NC
USX Corp. Texas City, TX	51	145			79	
TOTAL CAPACITY	18,930	13,650	1,195	6,050	14,040	
1990 Demand	13,500	N/A	N/A	N/A	N/A	
1991 Demand	N/A	N/A	950	5310	N/A	
1992 Demand	13,790	N/A	980	5440	N/A	
1993 Demand	14,150	N/A	N/A	N/A	N/A	
1996 Demand	N/A	N/A	1050	6010	N/A	

Sources:
Capacity data: *1992 Directory of Chemical Producers: United States of America*, SRI International
Demand Estimates: *Chemical Marketing Reporter*
N/A: Not Available

Abbreviations (apply to Benzene only):
CR: Catalytic Reformate   T: Toluene   PYG: Pyrolysis Gasoline   PC: Partly Captive Use
XIS: Xylene Isomerization   COLO: Coke-Oven Light Oil   NC: No Captive Use   FC: Fully Captive Use
Arco Chemical went bankrupt in 1993
Additional companies which began producing benzene in 1993 are: Marathon (51 million lb/yr) and Phibro (36 million lb/yr)

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TABLE 2.4   SUPPLY AND DEMAND OF 33/50 KETONES

Producer	Capacity[a,b] (million lbs/yr)		
	MEK	MIBK	Process
Exxon Chemical Co. Baton Rouge, LA	230	---	Dehydrogenation of sec-butyl alcohol
Hoechst Celanese Co. Pampa, TX	80	---	Butane oxidation
Shell Chemical Co. Norco, LA	230	---	Dehydrogenation of sec-butyl alcohol
Shell Chemical Co. Deer Park, TX	---	100	Captive acetone; co-product is MIBK
Tennessee Eastman Co. Kingsport, TN	---	45	Purchased acetone; co-product is DIBK
Union Carbide Institute, WV	---	80	Captive acetone; co-products are MIBK and DIBK
TOTAL	540	225	
1992 Demand	490	175	
1993 Demand	500	165	
1997 Demand	550	145	

Sources:

Capacity and demand information from *Chemical Marketing Reporter*

Process info: *1992 Directory of Chemical Producers: United States of America*, SRI International

[a] MEK capacities are flexible: Shell Chemical Company and Exxon Chemical Company can produce acetone as an alternative product, and Hoechst Celanese can emphasize production of acetic acid co-product. MIBK capacities probably include di-isobutyl ketone (DIBK) and methyl isobutylcarbinol (MIBC) co-products.

[b] Capacities may vary depending on product mix

billion pounds.[23] In 1992 capacity and consumption were 18.9 billion and 13.8 billion pounds, respectively. The demand for benzene is projected to grow 2.5 to 3.5 percent per year through 1997.[24] The supply and demand are expected to remain in balance provided that the demand for styrene and cyclohexane, two products manufactured from benzene, remains stable.[25]

The U.S. had the capacity to produce approximately 13.7 billion pounds of toluene in 1992.[26] Future fuel regulations and standards could influence the demand for toluene, one of the high octane components of gasoline. Although the octane requirements for gasoline are expected to increase, stricter controls on volatile organic compounds (VOCs) could eventually cause decreased demand for toluene in

fuel.[27] Since almost half of the toluene produced is used to manufacture benzene, the demand for benzene as a chemical raw material could also influence the market for toluene.

> *The future market for the 33/50 aromatics is linked to their use as chemical intermediates in the production of plastics and resins:*
>
> - *benzene is used to produce styrene and cyclohexane (used to produce nylon);*
>
> - *toluene is used to produce benzene;*
>
> - *o-xylene is used to produce phthalic anhydride (used to produce PET and alkyd resin); and*
>
> - *xylene is used to produce PET fibers and resins.*

The annual capacity of mixed xylenes producers in 1992 was 14 billion pounds.[28] The projected growth rate of p-xylenes is 4.5 percent per year through 1993, based on the strength of the dimethyl terephthalate and terephthalatic acid (DMT-PTA) market.[29] P-xylene is a chemical intermediate in the manufacture of DMT-PTA, which are used to produce polyethylene terephthalate (PET) fibers and resins. The estimated growth rate of o-xylene is 2.5 percent per year through 1993. The future for o-xylene is strongly tied to the production of phthalic anhydride because its production consumes about 90 percent of the o-xylene produced.[30]

Reformulated Gasoline. In April of 1992, EPA published a supplemental notice of proposed rulemaking on the standards and enforcement scheme for reformulated, conventional gasoline under the Clean Air Act (CAA). The notice supplemented the proposal for the reformulated gasoline program that was originally published in July of 1991. The proposed rulemaking is intended to meet the CAA requirements that: 1) gasoline sold in the nine worst ozone nonattainment areas be reformulated to reduce toxic and ozone-forming VOC emissions; and 2)

gasoline sold in the rest of the U.S. be prohibited from becoming more polluting than gasoline sold in 1990.

Among other things, the CAA requires that reformulated gasoline shall comply with the more stringent of a gasoline formula provided in the Act or performance standards. The reformulated gasoline formula limits benzene content to not more than one percent by volume, and total aromatic hydrocarbon content to not more than 25 percent by volume. The Act allows the EPA administrator to determine the composition of gasoline sold or introduced into commerce in 1990, but provides baseline gasoline fuel properties if no adequate or reliable data exist regarding the composition of gasoline in 1990. Among other components, the baseline gasoline defined in the Act contains 1.53 percent benzene and 32 percent aromatics. Clearly, implementation of the standards for reformulated gasoline will affect the chemical market for BTX compounds. A reduction in the concentration of BTX in gasoline may cause producers to place new emphasis on the use of these chemicals as chemical intermediates.

Ketones Market Trends

The U.S. produced 482 million pounds of MEK in 1988, with 424 million pounds being sold that same year (selling for a total value of $166 million).[31] Production capabilities and demand increased to 540 and 490 million pounds, respectively, in 1992.[32] The long term outlook for MEK is that its usage will decline by two percent per year as stricter VOC restrictions are introduced.[33]

Approximately 205 million pounds of MIBK were manufactured and 159 million pounds were sold in 1988 (selling for a total value of nearly $60 million).[34] For 1992 these figures increased to 225 and 175 million pounds, capacity and demand respectively.[35] Small amounts of this ketone can be formed as by-products of other processes, which can then be used on the plant site or sold for a modest profit. The long-term outlook is that usage of MIBK will decline slightly as stricter VOC legislation is passed.[36]

Price of the 33/50 Organic Compounds

The prices of the 33/50 organic compounds have fluctuated over the years. The price of the 33/50 aromatics are directly linked to the price of crude oil. Table 2.5 presents the historical price range and current prices. The current prices for each of the compounds are in the mid-to-upper historical price range. The price of MIBK is at its historical high.

PRODUCTION PROCESSES

BTX compounds are produced from petroleum and, less commonly, as a byproduct of the carbonization of coal to produce coke for the steel industry. MEK and MIBK are produced from sec-butyl alcohol and acetone, respectively. The following sections discuss processes for producing BTX from crude oil and manufacturing MEK and MIBK.

BTX Production Processes

Crude oil is composed primarily of paraffins, naphthenes, and aromatic compounds in varying proportions. Crude oil processing involves primary distillation followed by one or more of several conversion and/or upgrading processes to yield the desired final products. Figure 2.1 illustrates the products manufactured from crude oil and the estimated volume fraction of crude oil that is used to produce each product.[37] Finished gasoline, fuel oil, and jet fuel are by far the most dominant products of crude oil. Petrochemical feedstock, which is used to produce BTX and other chemicals, comprises approximately three percent by volume of the products of crude oil.

The two most common sources of BTX from petroleum are the catalytic reforming process and pyrolysis gasoline. Portions of the toluene and xylene from these sources are also used as feed streams to additional processes to produce benzene. Figure 2.2 depicts the sources of BTX derived from crude oil.[38] Table 2.6 lists the production capacity for BTX compounds by the most commonly employed processes.

Catalytic Reforming. Catalytic reforming is a platinum-catalyzed, high temperature (470 to 530°C) process in which nonaromatic hydrocarbons are converted to an aromatic product called reformate. The feed stream to the reforming process, petroleum feedstock of Figure 2.1, consists of C_6 to C_{12} hydrocarbons in the 70 to 190°C boiling range (e.g., light petroleum distillate or straight run naphtha).

TABLE 2.5   PRICES OF 33/50 ORGANIC COMPOUNDS

| Chemical | Historical ($/lb)[a] | | Current ($/lb)[b] |
	High	Low	
Benzene	2.25	0.21	.85
Toluene	N/A	N/A	0.67
o-Xylene	0.26	0.03	0.155
p-Xylene	0.33	0.0625	0.23
MEK	0.50	0.0925	0.40
MIBK	0.51	0.12	0.51 to 0.53

Source:

Chemical Marketing Reporter

[a] Historical price range is from 1964-1989 for Benzene, MEK, and MIBK; from 1964-1989 for o-Xylene; and from 1973-1989 for p-Xylene

[b] Current price for industrial grade, bulk quantity, as of week ending February 4, 1994

N/A: Not Available
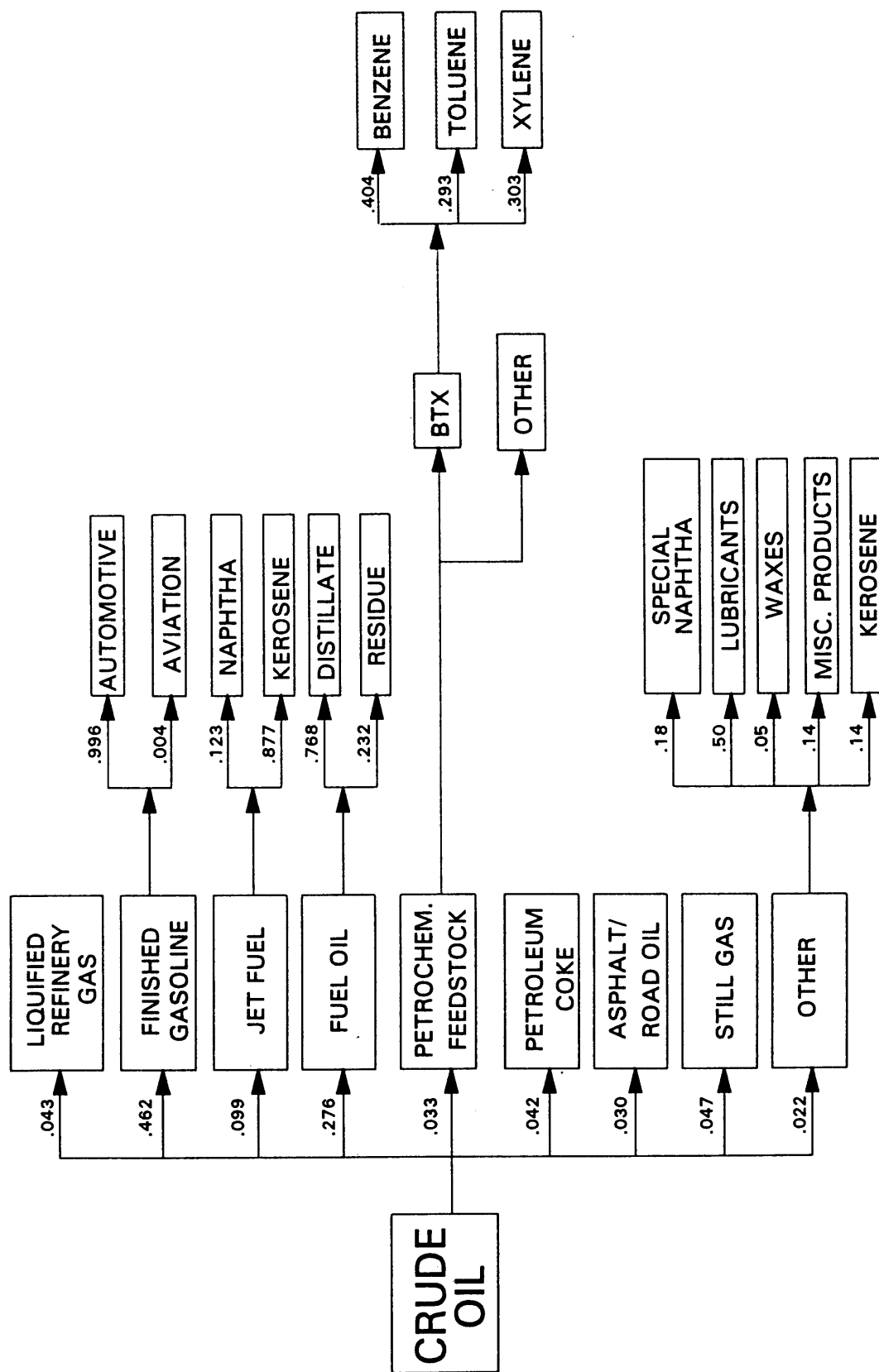
FIGURE 2.1   PRODUCTS MANUFACTURED FROM CRUDE OIL

NOTE: All values in volume fractions. Data were not available to estimate the volume fraction of petrochemical feedstock used to manufacture BTX and/or the "other" category.
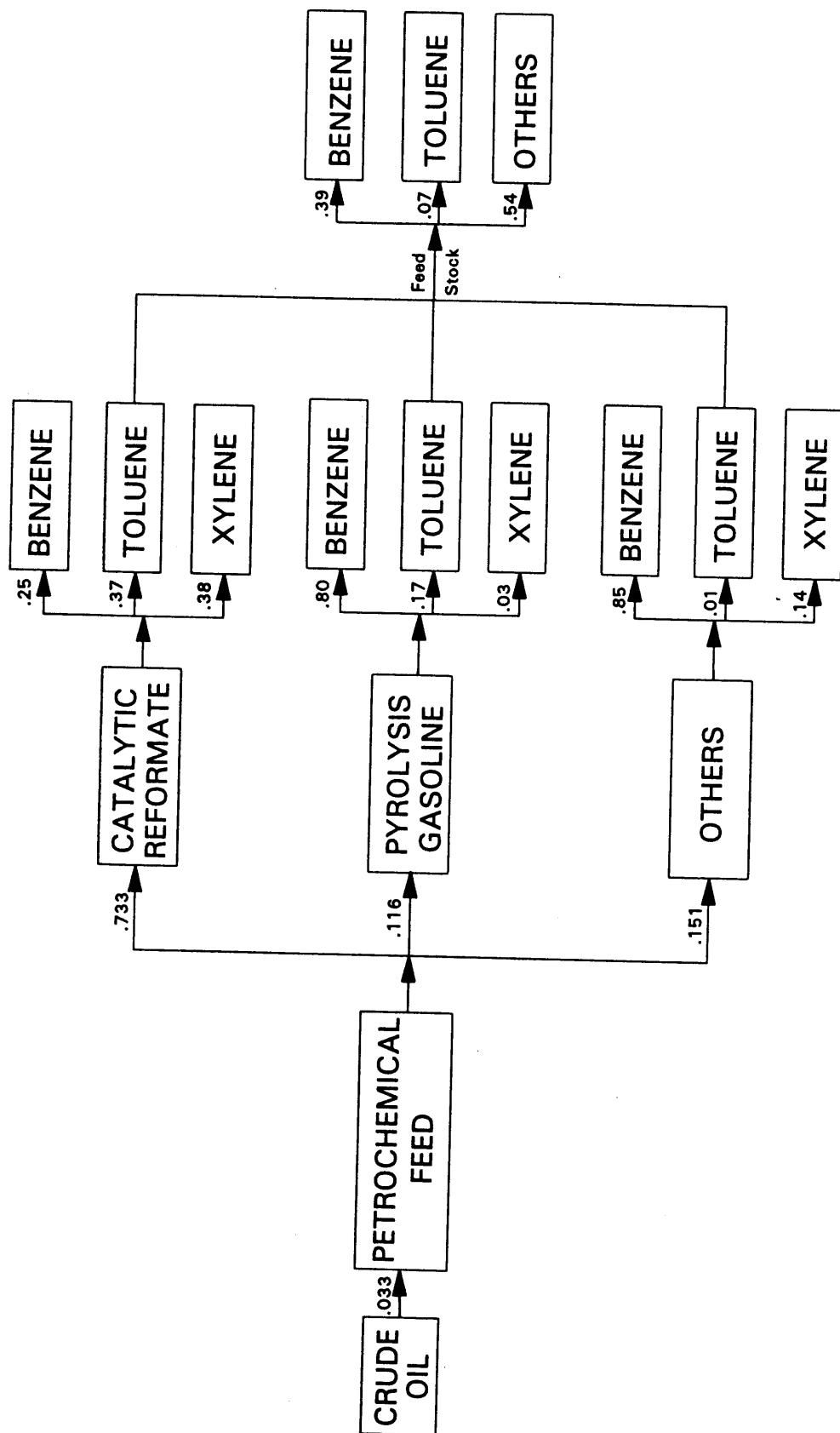
FIGURE 2.2   PRODUCTION OF BTX FROM CRUDE OIL

NOTE: A small amount of BTX is produced from coke-oven light oil.

TABLE 2.6   PRODUCTION CAPACITY OF BTX COMPOUNDS BY PROCESS CAPACITY

Chemical	Production Capacity (million lb)					
	Catalytic Reformate	Pyrolysis Gasoline	Toluene Feed	Coke Oven Light Oil	Xylene Isomerization	Total
Benzene	8,576	4,346	5,398	450	160	18,930
Toluene	12,657	904	---	59	29	13,650
Mixed Xylenes	12,882	187	948	22	---	14,040
TOTAL BTX	34,120	5,437	6,346	531	189	46,620

Source:
1992 Directory of Chemical Producers: United States of America, SRI International

The composition of these streams varies with the source of the crude oil resulting in a variable reformate composition; more C_6 to C_8 nonaromatics result in more benzene and toluene. Pretreatment prior to catalytic reforming is required to remove impurities of sulfur, nitrogen, and oxygen. Chemical reactions involved in catalytic reforming may include dehydrogenation of naphthenes to aromatics, dehydrocyclization of paraffins to aromatics, or isomerization of alkylnaphthenes followed by dehydrogenation.[39]

Typical ratios of reformate BTX concentrations are approximately 1:4:5, benzene:toluene:xylene, with the fraction of BTX near 60 percent of reformate. A large portion of the remaining 40 percent of the reformation product, between 18 to 35 percent, contains nonaromatics. These nonaromatics are removed by an extraction process, which leaves benzene, toluene, and C_8 and C_9+ aromatics. The aromatics are preferentially dissolved and separated from the nonaromatic compounds, and recovered by distillation.[40]

The aromatic content of the reformate is not only dependant on the composition of the feed, but also directly related to the severity of catalytic reforming (e.g., temperature and process time); increasing the severity increases the aromatic concentration of the product. An increase in the concentration of BTX compounds enhances the octane level of gasolines, and thus increases the research octane number (RON). The RON is used to indicate the relative degree of reforming severity. In this manner, BTX processing and the gasoline production industry are closely linked. The removal of BTX from gasoline pools for chemical processing can thus influence the cost and performance of gasoline.[41]

Pyrolysis Gasoline. Pyrolysis gasoline, or dripoline, is another source of BTX. Pyrolysis gasoline is produced as a by-product from the high-temperature, short-residence time cracking of paraffin gases, naphthas, gas oils, or other hydrocarbons in the production of ethylene. The quantity of pyrolysis gasoline produced from the cracking of crude oil fractions is a function of feedstock and operating conditions, and is increased when heavier charge stocks are used.[42] A larger yield of toluene and xylene, relative to benzene, is produced by increasing the boiling point of the feed.

The BTX content of pyrolysis gasoline is greater than 60 percent. Pyrolysis gasoline

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also contains other unsaturates and diolefins (> 5 percent) which cause instability in the BTX product. If used as an aromatic product, this instability problem is controlled by a two-stage process; stage one involves the conversion of diolefins to olefins by hydrotreatment, stage two is the saturation of the olefins. [43]

Toluene Feed. The disproportionate production of toluene over benzene in catalytic reformation requires additional processing to create more benzene, the higher valued product. Two processes are utilized to convert toluene and other low weight aromatics to benzene and xylene; disproportionation and hydrodealkylation. Disproportionation is an equilibrium reaction where toluene is used to produce benzene and xylene isomers. In the disproportionation reaction, a methyl group is transferred from a molecule of toluene to a second molecule of toluene to yield one molecule of benzene and one molecule of xylene. Operating temperatures range between 350 and 525°C. Hydrodealkylation may be purely thermal or catalyzed by metals or supported metal oxides. Typical catalytic reaction conditions include an operating temperature between 575 to 650°C, an elevated pressure, and a chromium-alumina or platinum-alumina catalyst in the presence of hydrogen. The thermal process is carried out under higher temperatures without a catalyst present. Both processes are used to manufacture benzene of high purity and xylenes containing less than one part per billion of saturated hydrocarbons. [44]

Separation of Mixed Xylenes. Mixed xylenes may be separated into the different xylene isomers by the following processes:

- o-xylene may be separated from m-xylene by a two stage distillation column, as the boiling points of these isomers differ by approximately 5°C; [45] or

- p-xylene may be separated from the mixed isomers by a crystallization or adsorption

process because it has a significantly higher freezing point than the other isomers. [46]

Generally, the individual isomers are isolated from mixed xylenes through further steps including distillation, fractionation, crystallization, adsorption, and solvent extraction.

Ketone Production Processes

The vapor-phase dehydrogenation of sec-butyl alcohol, used to produce approximately 85 percent of the MEK in the U.S., is similar to the manufacture of acetone from isopropanol. The first step in this two-step process is the hydrogenation of butenes to 2-butanol by mixing with aqueous sulfuric acid. Then the 2-butanol is dehydrogenated with a zinc- or copper-based catalyst at high temperatures (400 to 500°C) and low pressures (less than 3.4 atmosphere). [47] Another source for MEK is as a by-product of liquid-phase oxidation of butane to acetic acid. Hoechst Celanese in Pampa, Texas reportedly uses this process to produce MEK.

The most common method for the production of MIBK is the conversion of acetone in three steps. The first step consists of a liquid-phase condensation of acetone in an alkaline fixed bed reactor. This produces diacetone alcohol, which is then dehydrated by an acid-catalyzation procedure at 100°C. The resulting mesityl oxide is selectively hydrogenated over a nickel catalyst. [48] Other catalysts that can be used effectively for this third step are copper, nickel-chromium, and palladium.

Another commercially feasible method for the production of MIBK is the Hibernia Schölven process. Dilute sodium hydroxide and acetone are fed to a reactor which is allowed to run until the reaction has been completed. Phosphoric acid is then added to stabilize the product which is sent to the first column to remove the remaining acetone. More phosphoric acid is added to the resulting diacetone alcohol bottoms mixture and is fed to

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the dehydrating column. The head mixture of this second column is mostly mesityl oxide and is purified to 98 percent in the third column. The fourth and last column is where the mesityl oxide is hydrogenated over a palladium catalyst to form MIBK.[49]

ENVIRONMENTAL RELEASES OF THE 33/50 ORGANIC COMPOUNDS

Environmental releases of the 33/50 organic compounds occur from their production, use, and disposal. The types of releases and transfers that occur from production facilities and the releases and transfers reported by the major producers of these chemicals in the 1991 TRI are discussed below. Also presented is the distribution of environmental releases by industry group.

Environmental Releases from Production Facilities

Air emissions of organic compounds from production processes can originate from the continuous or intermittent purging of inert gases from reactor vessels, drying beds, finishing columns, and other process vessels. Fugitive air emissions result when process fluid leaks from plant equipment such as pumps, compressors, process valves, and other equipment. Air emissions from storage and handling operations also occur at production facilities. Other sources of environmental releases or transfers include the following:

■ wastewater discharges directly from the plant into rivers, streams, or other bodies of water, or transfers to a publicly owned treatment works (POTW);

■ on-site release to landfills, surface impoundments, land treatment, or another mode of land disposal;

■ disposal of wastes by deep-well injection; and,

■ transfers of wastes to off-site facilities for treatment, storage, or disposal.

Aromatic Compounds. Table 2.7 presents the releases and transfers of BTX compounds from petroleum refining (SIC 2911) reported in the 1991 TRI. These releases and transfers are an overstatement of the releases and transfers that would result simply from petrochemical feed production, but they are an indicator of the large volume of BTX released and transferred at the front end of the petroleum products manufacturing process. Using the principles of life cycle assessment and assuming that about three percent of crude oil is used to manufacture petrochemical feedstock (see Figure 2.1), about three percent of these releases (740 thousand pounds of BTX) can be attributed to petrochemical feed production.

Environmental releases of BTX from production occur from the initial distillation of crude oil through the various production processes outlined above. However, the primary releases from the conversion of crude oil into petroleum products are nonaromatic organic compounds (the light and heavy reformate from distillation column) and the solvents used in the extraction vessels. The used solvent is usually recovered or recycled and the nonaromatic compounds can be distilled based on their different boiling points. Thus the light or heavy reformates can be used or disposed depending on their characteristics.

Ketones. The environmental releases and transfers of MEK and MIBK from the major producers identified in Table 2.3, plus releases and transfers from producers that were active in 1991 but have since shut down their plants, were retrieved from the 1991 TRI database. The data are presented in Table 2.8. Many of the facilities reported multiple SIC codes on one form, indicating the data may include releases from internal use of the chemicals after production.

TABLE 2.7   RELEASES AND TRANSFERS OF BTX COMPOUNDS FROM PETROLEUM REFINING (SIC 2911)

Chemical	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Benzene	4,377,043	14,783	95,481	89,376	4,576,683	214,837	71,070	285,907
Xylenes (mixed isomers)	5,376,962	11,815	110,810	23,284	5,522,871	164,746	114,115	278,861
m-Xylene	318,988	925	2,920	5	322,838	1,178	9,648	10,826
o-Xylene	285,334	1,181	1,348	5	287,868	715	7,385	8,100
p-Xylene	647,406	765	1,569	5	649,745	748	5,071	5,819
Toluene	9,988,596	32,066	49,600	81,926	10,152,188	254,209	76,169	330,378
TOTAL	20,994,329	61,535	261,728	194,601	21,512,193	636,433	283,458	919,891

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

TABLE 2.8   RELEASES AND TRANSFERS OF KETONES FROM PRODUCTION FACILITIES

	Releases and Transfers (lbs/yr)							
MEK Producer	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Arco Chemical, Channel View, TX	14,920	0	0	78,620	93,540	N/A	55,130	55,130
Exxon Chemical, Baton Rouge, LA	36,000	100	0	0	36,100	N/A	26	26
Hoechst Celanese, Pampa, TX	77,000	0	0	0	77,000	0	500	500
Shell Chemical, Norco, LA	85,000	0	370	0	85,370	N/A	3	0
TOTAL	212,920	100	370	78,620	292,010	0	55,659	55,659
MIBK Producer								
Shell Oil, Deer Park, TX	36,968	0	96	0	37,064	0	0	0
Eastman Kodak Co., TN Eastman Division, Kingsport, TN	240,000	1,200	29	0	241,229	N/A	0	0
Union Carbide, Institute, WV	146,495	178	9	0	146,682	N/A	0	0
TOTAL	423,463	1,378	134	0	424,975	0	0	0

Source:
TRI, 1991

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Distribution of Environmental Releases by Industry Group

Each of the 33/50 organic chemicals were within the top 40 chemicals for TRI total releases and transfers in 1991. Table 2.9 lists their total releases and transfers and relative rank. Toluene contributed the largest percentage of total emissions for this chemical class, accounting for 42 percent of the total releases and transfers of the 33/50 organic chemicals.[50]

Releases and transfers of the 33/50 organic compounds were fairly widely distributed across industry groups in 1991. The top seven industries that emitted the largest quantities of 33/50 organic compounds and their total reported releases and transfers are listed in Table 2.10. The chemicals and allied products industry, which includes plastics and resins manufacturers, reported the largest total emissions of the 33/50 organic compounds, followed by the transportation industry and companies that listed multiple SIC codes. Releases from the chemicals and allied products industry result from using the compounds as chemical intermediates, as solvents, and as chemical processing aids. Releases from the transportation industry can probably be largely attributed to the use of these materials as solvents in paints and coatings and as cleaning solvents.

Environmental releases and transfers of the 33/50 organic chemicals were widely distributed across industry groups in 1991. The chemicals and allied products industry reported the greatest releases of benzene, toluene, and m-, o- and p-xylene, probably from their use as chemical intermediates, solvents, and chemical processing aids. Rubber and plastic products manufacturers reported the largest releases of MEK; manufacturers of transportation equipment had the greatest releases of MIBK and mixed xylenes.

USES OF THE 33/50 ORGANIC CHEMICALS

The BTX compounds are widely used as chemical intermediates in the manufacture of plastics and resins and other chemicals and as solvents. The primary use of MEK and MIBK is as a coatings solvent. The uses are illustrated in chemical-use tree diagrams. Figure 2.3 presents the uses of benzene to produce major chemical intermediates.[51] Figures 2.3.1 through 2.3.4 present the products manufactured from the major chemical intermediates.[52]

TABLE 2.9   TOTAL RELEASES AND TRANSFERS OF 33/50 ORGANIC CHEMICALS

Chemical	Releases and Transfers (lbs/yr)	TRI Rank
Toluene	223,500,172	5
Mixed Xylenes (all)	146,677,780	9
MEK	114,870,964	11
MIBK	30,795,824	30
Benzene	20,860,044	37
TOTAL	536,704,784	

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

TABLE 2.10 TOP INDUSTRIES FOR TOTAL TRI RELEASES AND TRANSFERS OF 33/50 ORGANIC COMPOUNDS

Chemical	Releases and Transfers (lbs/yr)[a]						
	Furniture SIC 25	Paper SIC 26	Printing SIC 27	Chemicals SIC 28	Plastics[c] SIC 30	Transport. SIC 37	Multiple Code SIC 20-39
Benzene	0	2,615	0	7,005,238	0	72,846	2,627,213
Methyl Ethyl Ketone	5,262,159	6,406,306	2,764,567	10,210,963	15,452,052	11,265,192	23,424,377
Methyl Isobutyl Ketone	2,224,593	618,700	273,984	7,234,991	2,518,081	7,326,081	2,061,113
Toluene	15,947,408	26,781,689	32,964,832	39,819,260	21,005,665	10,673,442	19,703,071
Xylene (Mixed Isomers)	10,688,332	1,950,299	1,934,788	25,414,938	5,275,239	30,345,990	8,838,484
m-Xylene	15	0	0	375,450	0	27,709	796,379
o-Xylene	1,000	0	0	1,207,899	0	18,127	473,777
p-Xylene	0	0	0	4,216,194	0	8,940	468,597
TOTAL RELEASES AND TRANSFERS	34,123,507	35,759,609	37,938,171	95,484,933	44,251,037	59,738,327	58,393,011
PERCENT OF TOTAL RELEASES AND TRANSFERS[a]	6.35	6.66	7.06	17.79	8.24	11.13	10.88

Sources:
TRI, 1991
Correspondence from Hampshire Research Association, Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office
[a] Based on 1991 data
[b] Total for these organic chemicals in all industry groups in 1991 was 536,704,784 lbs.
[c] Rubber and plastic product manufacturers

Figure 2.4 presents the uses of toluene and its major chemical intermediate, toluene-diisocyanate.[53] Figure 2.5 is the chemical-use tree for xylene.[54] Figures 2.6 is the chemical-use tree diagram for MEK and MIBK.[55]

The 33/50 aromatics are the basic building blocks of many of the plastics and resins in use today. Toluene, xylene, MEK, and MIBK are widely used as solvents in paints and coatings. These use clusters were selected for substitutes evaluation.

The numbers along each branch of the chemical-use tree are weight fractions of the usage of the chemical or product in the first box to produce the chemical or product in the second box. For example, in Figure 2.3, 53 percent of the benzene produced is used to manufacture ethylbenzene; 99 percent of the ethylbenzene produced is used to produce styrene monomer.

Many of the 33/50 organic chemicals are used to produce variations of a similar product, i.e., use clusters. Plastics and resins, and paint and coating solvents are the two use clusters which have the broadest applications or uses of these chemicals. Consequently, these use clusters were selected for evaluation of substitutes and are discussed briefly below.

Plastics and Resins

Benzene, toluene, and the xylene isomers are the basic building blocks of many of the myriad plastics and resins in widespread use today. Cyanide compounds and dichloromethane, two other 33/50 chemicals,

are also used to produce certain plastics and resins. Further, some of the 33/50 metals are used as pigments in consumer products made from plastics and resins. The evaluations in Chapter 7 focus on safe substitutes for products made from the styrene monomer that is manufactured from benzene. A side benefit of reductions in the use of certain plastics and resins to reduce BTX releases could be a reduction in the use of toxic inorganic pigments.

Paints and Coatings

Toluene, xylene, MEK, and MIBK are widely used as solvents or diluents in paints and coatings, including industrial or consumer grade materials. Solvents provide several functions in paints and coatings, the most important of which is to decrease the coating's viscosity so that it may be applied in a thin film to the substrate. The 33/50 organic chemicals are widely used because they have good solvency power for a wide variety of the resins used in paints and coatings.

In consumer applications all the solvent in a paint is released to the atmosphere. In industrial applications control technologies are typically employed to reduce the release of these toxic chemicals to the environment, but releases and transfers still occur in substantial amounts. In both applications, workers may be exposed to the chemical by inhalation as it evaporates. With increased concern about the effects on worker safety and on the environment, substantial progress has been made in developing new low-solvent paint formulations, like water-borne paints or powder coatings. The substitutes analysis in Chapter 8 examines and evaluates these new, safer substitutes.
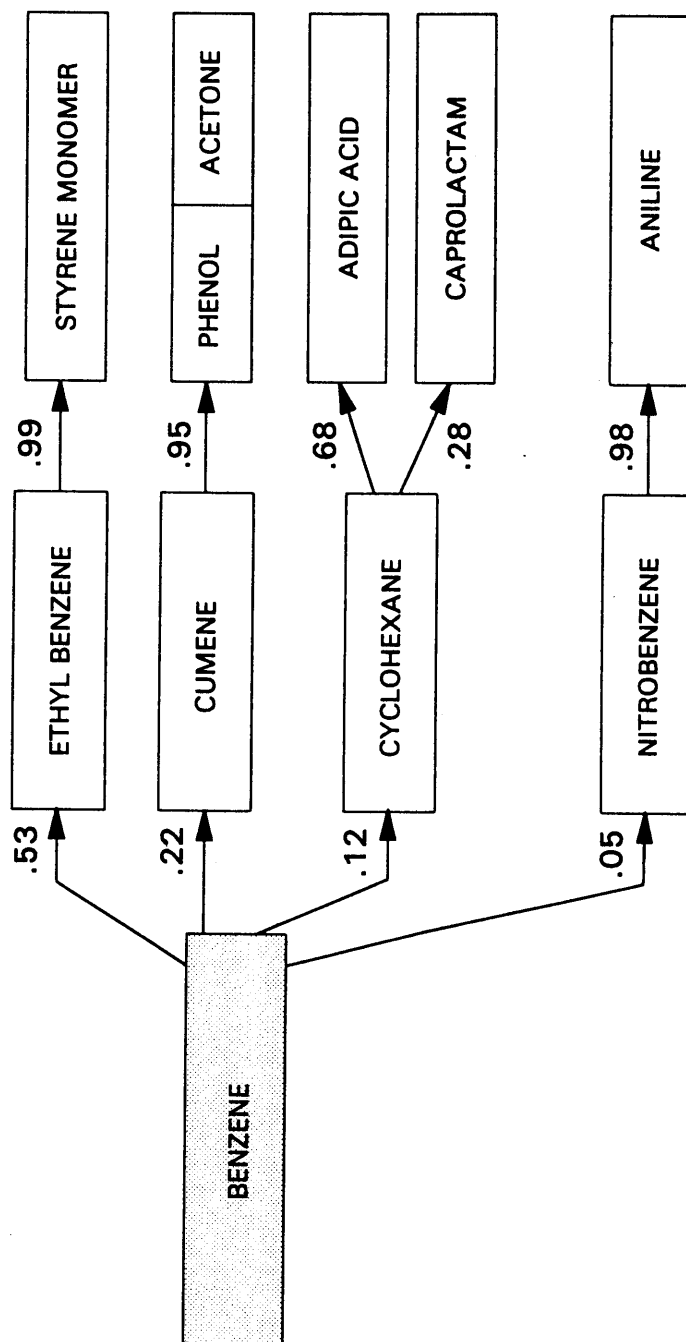
FIGURE 2.3   BENZENE TO MAJOR INTERMEDIATES
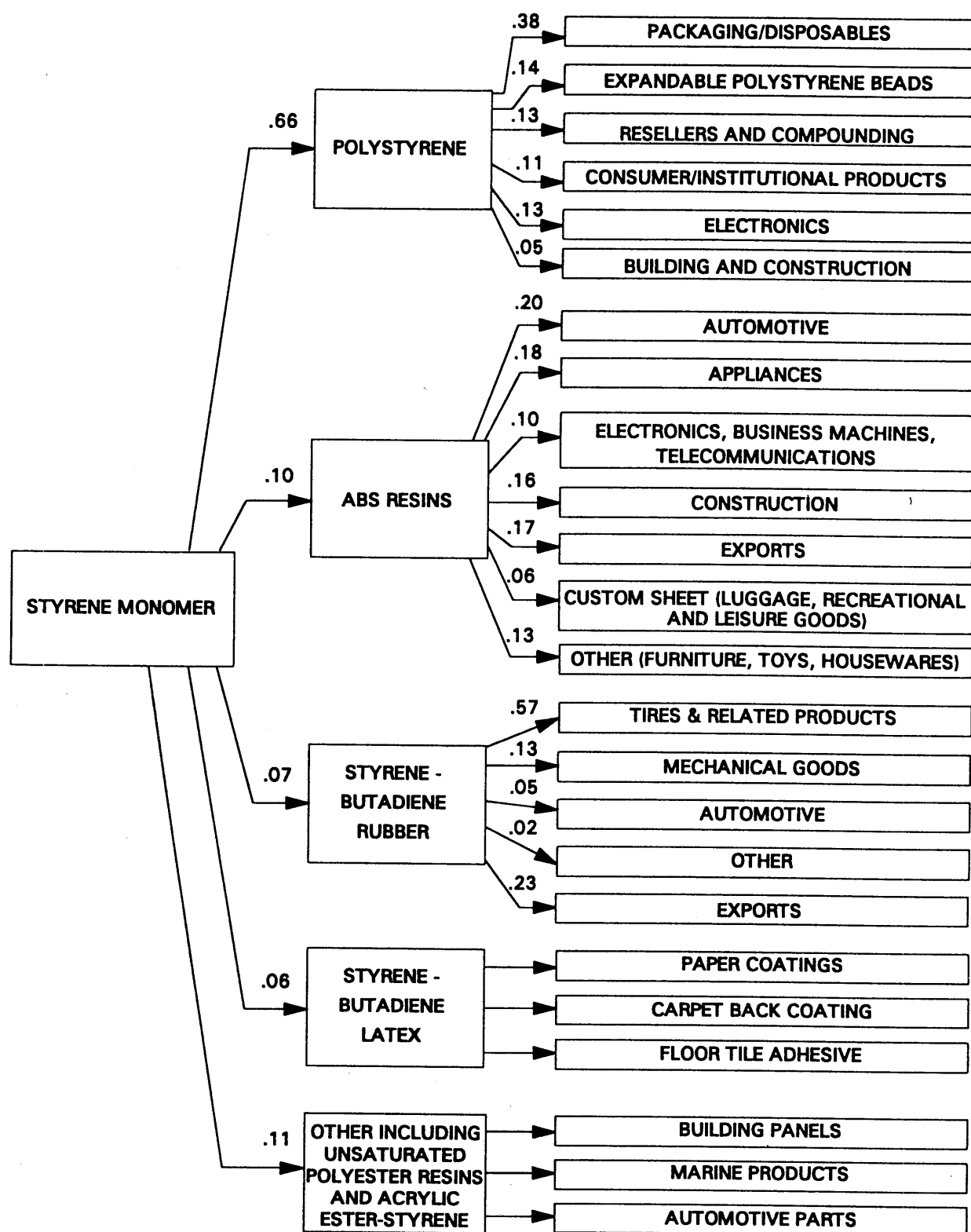
FIGURE 2.3.1   BENZENE - STYRENE MONOMER PRODUCTS

NOTE: Reliable data were not available to estimate weight fractions along some branches of the chemical-use tree

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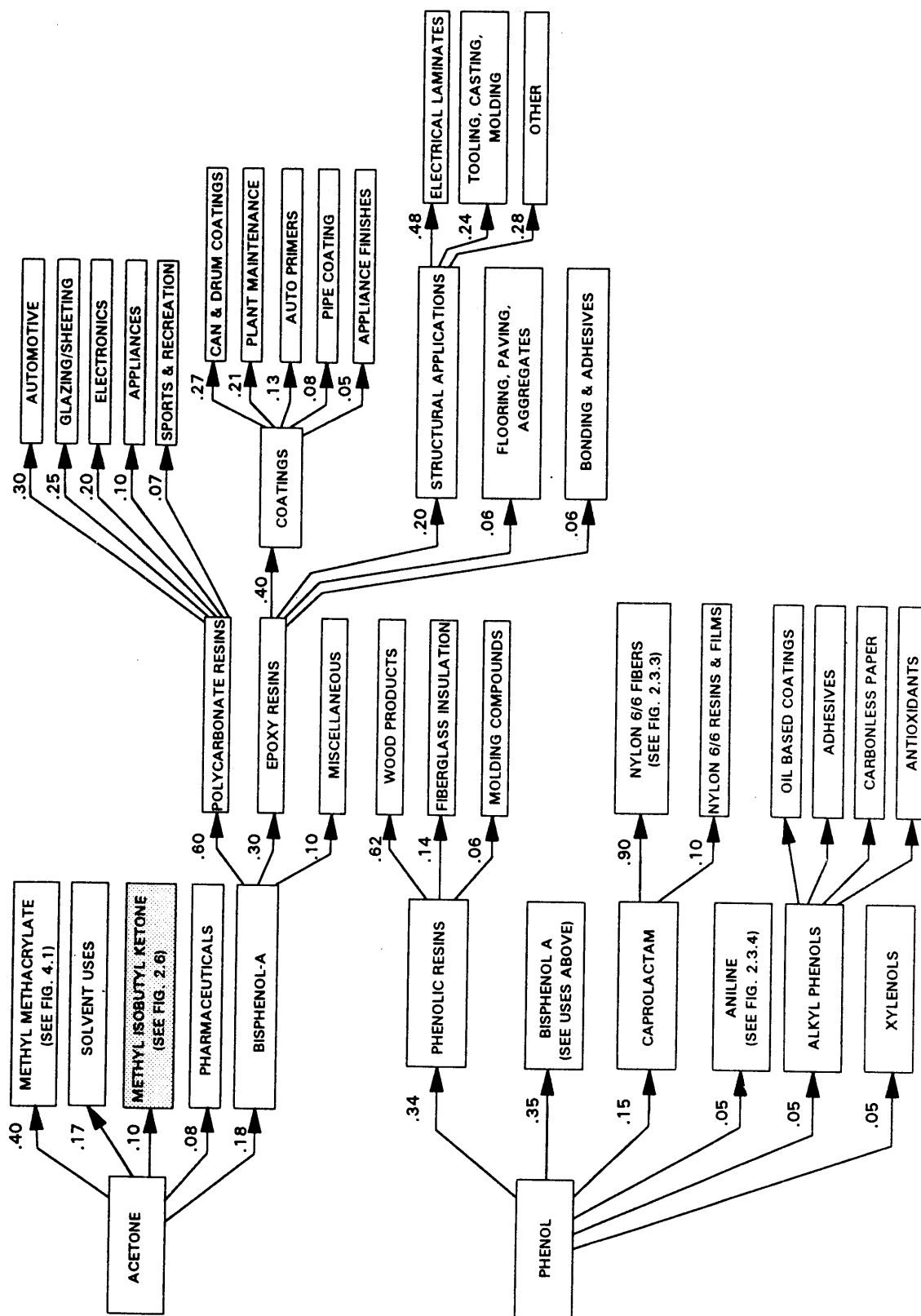
FIGURE 2.3.2   BENZENE - PHENOL/ACETONE PRODUCTS

NOTE: Reliable data were not available to estimate weight fractions along some branches of the chemical-use tree
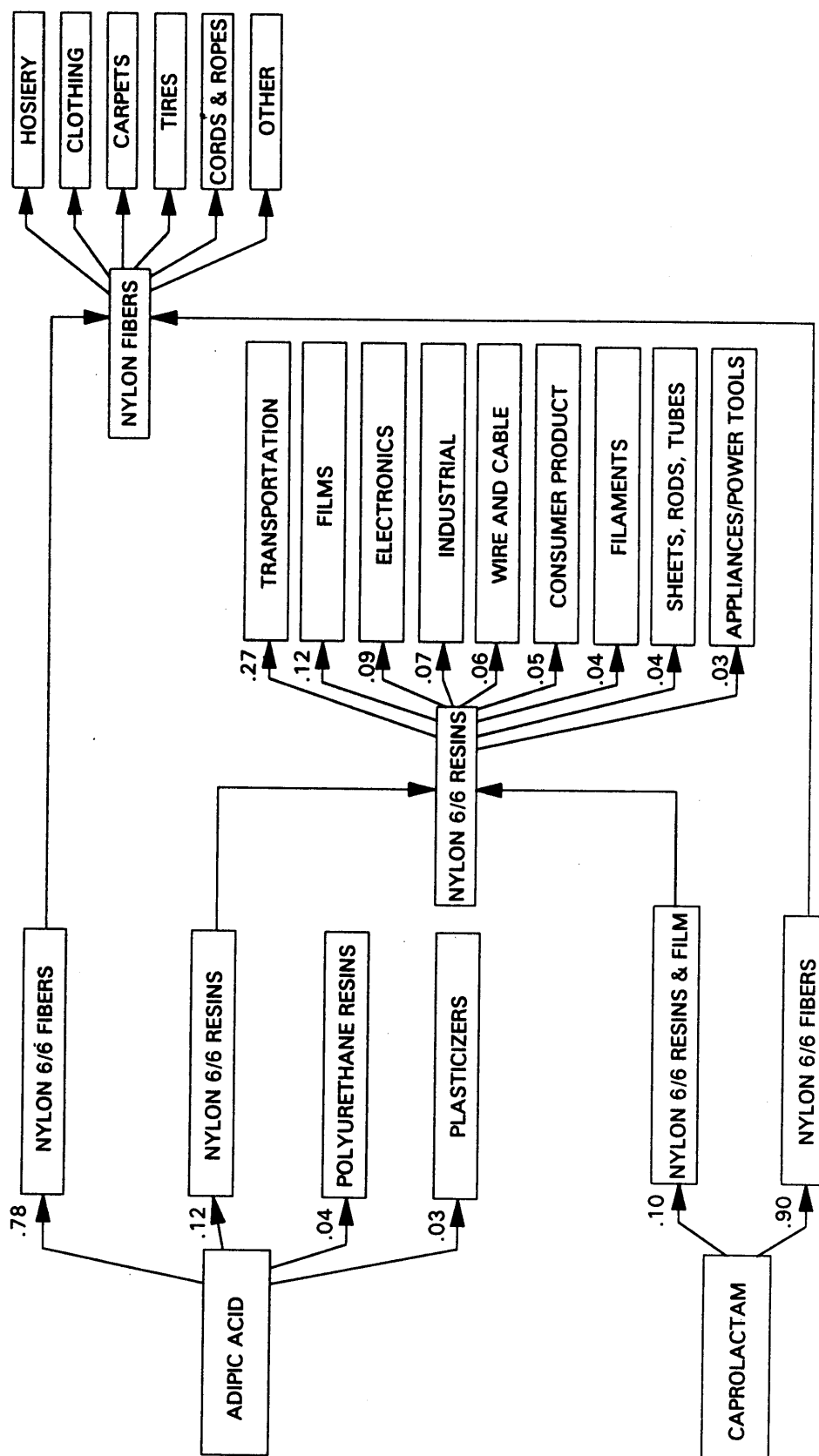
FIGURE 2.3.3   BENZENE - ADIPIC ACID/CAPROLACTAM PRODUCTS

NOTE: Reliable data were not available to estimate weight fractions along some branches of the chemical-use tree
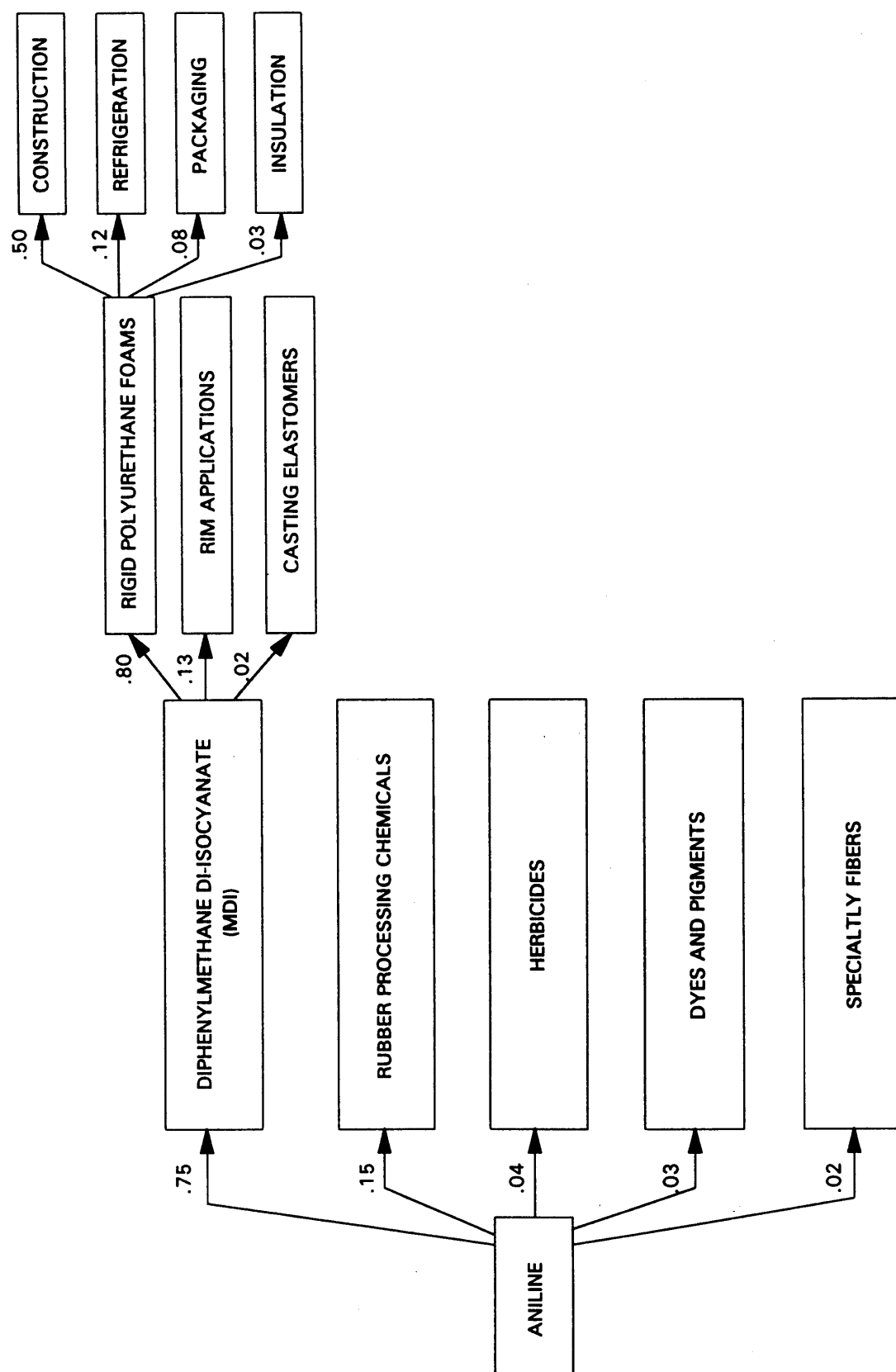
FIGURE 2.3.4   BENZENE - ANILINE PRODUCTS

FIGURE 2.4 TOLUENE

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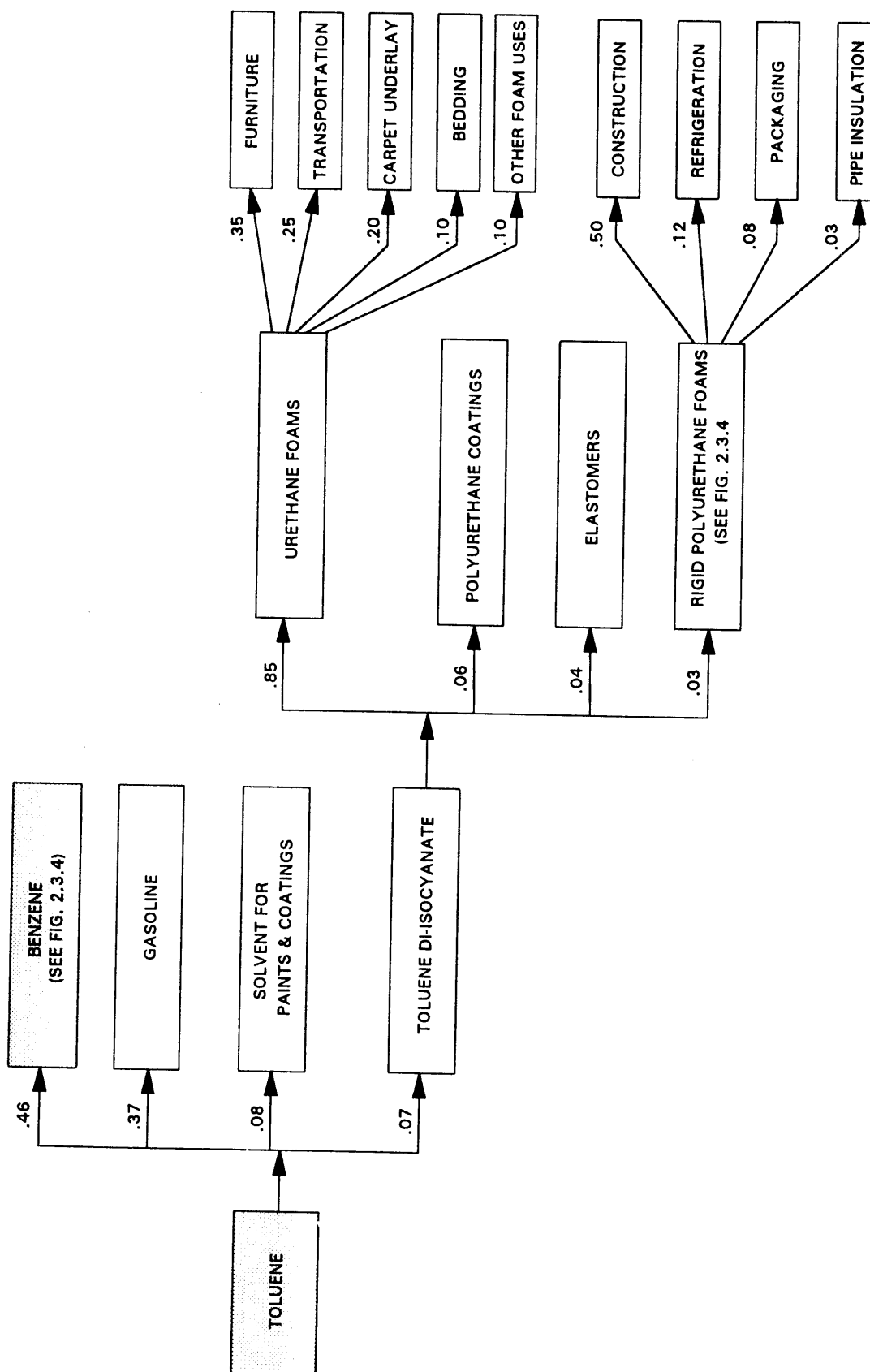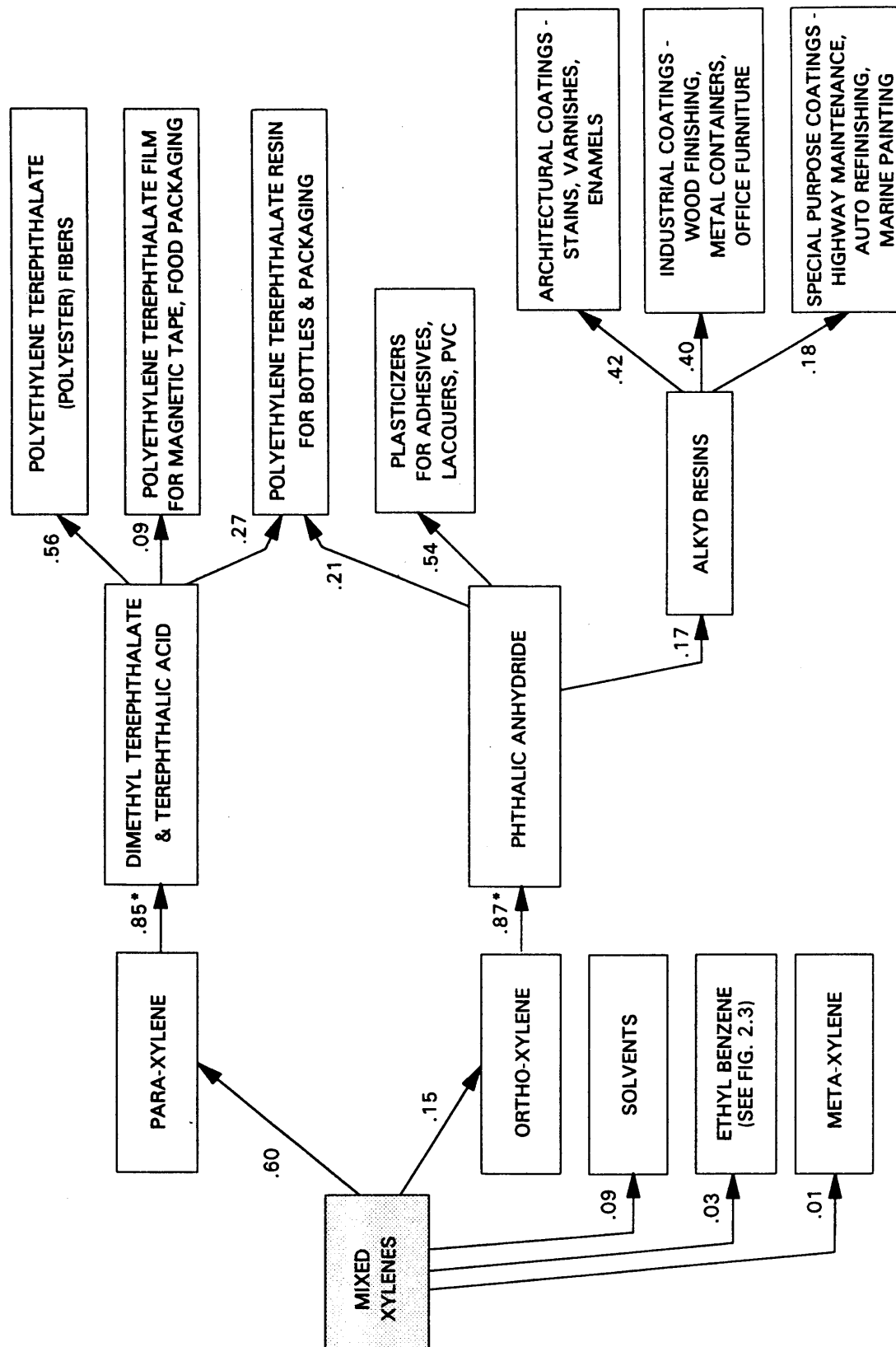
FIGURE 2.5   XYLENES

* Weight fractions of p-xylene and o-xylene to chemical intermediates are from 1989 data. Chemical profiles published in *Chemical Marketing Reporter* in 1992 state "virtually all" and "nearly all" of these isomers are used to produce the chemical intermediates.

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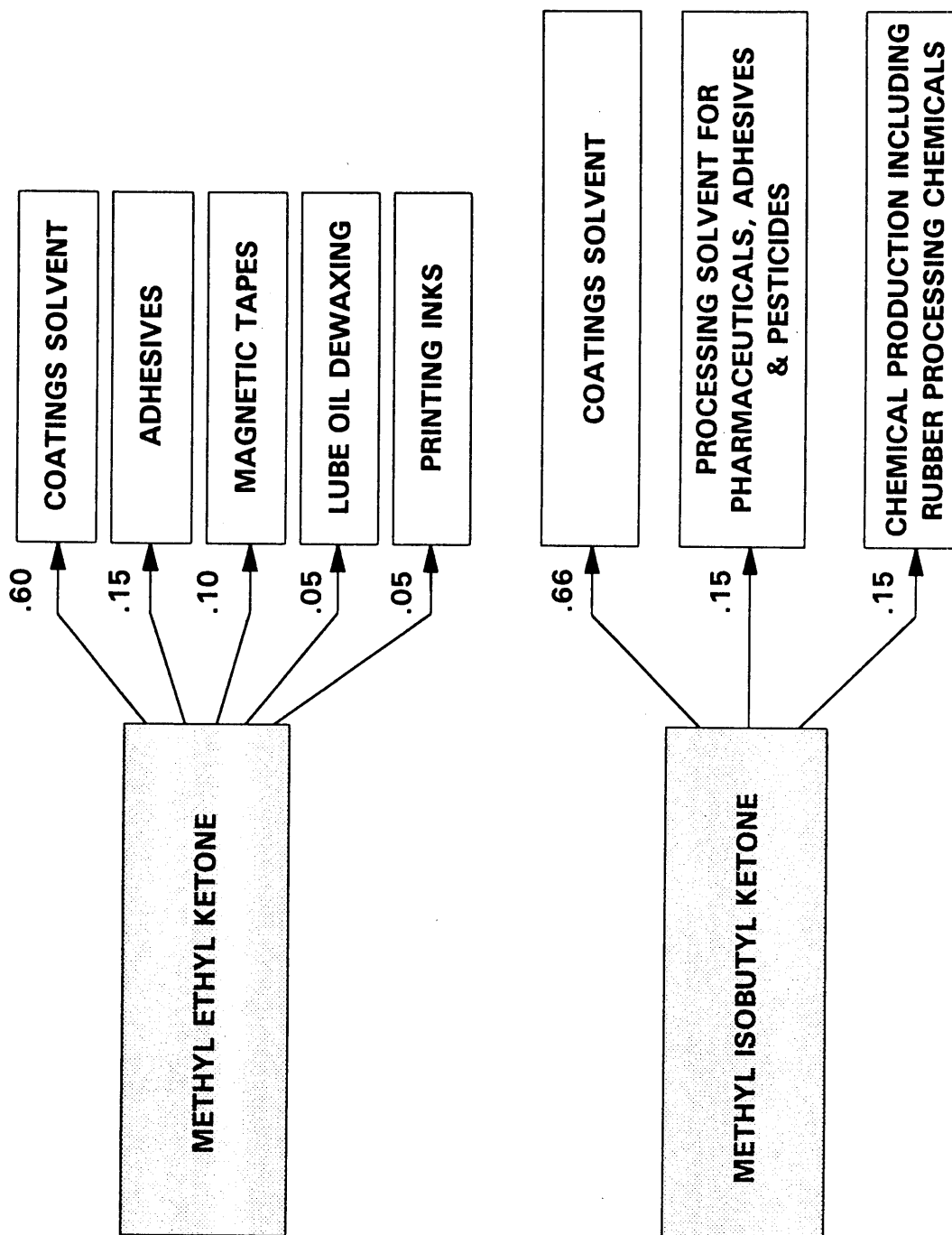
FIGURE 2.6   METHYL ETHYL KETONE and METHYL ISOBUTYL KETONE

ENDNOTES

[1] *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., (Weinham: VCH Verlag., 1985), Vol. A3.

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[3] *Kirk-Other Encyclopedia of Chemical Technology*, 3rd ed., (New York: John Wiley, 1978), Vol. 24.

[4] *Xylene: Chemical Information Sheet*, Illinois Environmental Protection Agency, Office of Chemical Safety, January 1989.

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[15] "o-Xylene," *Hazardous Substances Data Bank*, October 22, 1990.

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[33] "Chemical Profile: Methyl Ethyl Ketone," *Chemical Marketing Reporter*, August 27, 1990.

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[35] "Chemical Profile: Methyl Isobutyl Ketone," *Chemical Marketing Reporter*, August 2, 1993.

[36] "Chemical Profile: Methyl Isobutyl Ketone," *Chemical Marketing Reporter*, August 20, 1990.

[37] Sources for Figure 2.1:
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[54] Sources for Figure 2.5:
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"Chemical Profile: Orthoxylene," *Chemical Marketing Reporter*, August 3, 1992.
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CHAPTER 3

HALOGENATED ORGANIC COMPOUNDS

The six halogenated organic compounds on EPA's 33/50 list are dichloromethane (methylene chloride or DCM), chloroform (CFM), carbon tetrachloride (CTC), 1,1,1-trichloroethane (TCA), trichloroethylene (TCE), and tetrachloroethylene (perchloroethylene or PCE). Each of these compounds is primarily a synthetic substance, although DCM and CFM occur naturally in small amounts.

These 33/50 compounds belong to two distinct families of chemical compounds. DCM, CFM, and CTC belong to the family commonly known as the chloromethanes. TCA, TCE, and PCE are chlorinated ethanes and ethylenes.

PHYSICAL PROPERTIES

The 33/50 halogenated organic compounds share several common physical features. They are volatile, colorless, nonflammable liquids characterized by a sweet or ether-like odor. Their high chlorine content gives their liquids and vapors relatively high density and also reduces their ability to support combustion. They are subject to decomposition by hydrolysis with water and by high temperatures, oxygen, and sunlight. They are only slightly soluble in water and are miscible with most organic liquids. Table 3.1 shows selected physical properties and the chemical formulae of these compounds.

DCM is only slightly soluble in water, and is completely miscible with other grades of chlorinated solvents, diethyl ether, and ethyl alcohol. It also dissolves in most other common organic solvents. DCM, in its pure form, exhibits no flash point, but it will have a flash point if small amounts of other volatile solvents are added. DCM is one of the more stable of the chlorinated hydrocarbons, with its initial thermal degradation beginning at 120°C in dry air. This temperature decreases as the moisture content increases.[1]

CFM is miscible with the principal organic solvents and slightly soluble in water. It dissolves alkaloids, cellulose acetate and benzoate, ethyl cellulose, essential oils, fats, halogens, methyl methacrylate, many resins,

TABLE 3.1   SELECTED PROPERTIES OF 33/50 HALOGENATED COMPOUNDS

Property	DCM	CFM	CTC	PCE	TCE	TCA
Chemical Formula	CH₂Cl₂	CHCl₃	CCl₄	C₂Cl₄	C₂HCl₃	C₂H₃Cl₃
CAS No.	75-09-2	67-66-3	56-23-5	127-18-4	79-01-6	71-55-6
Molecular Weight	84.92	119.38	153.82	165.83	131.39	133.05
Boiling Point, at 101.3kPa, °C	39.8	61.3	76.72	121.20	86.7	74.00
Freezing Point, °C	-96.7	-63.2	-22.92	-22.7	-87.1	-33.00
Specific Gravity, at 20°C	1.320	1.50	1.595	1.62260	1.465	1.325
Density, at 20°C, kg/m³	1,315.7	1,500.0	1,594.0	1,622.4	1,460.0	1,324.9
Viscosity, at 20°C, cP	0.43	0.563	0.965	0.870	0.58	0.858
Heat of Vaporization at 20°C, kJ/kg	329.23	247ᵃ	194.7ᵃ	209.2ᵃ	240ᵃ	248.11
Heat Capacity at 25°C, kJ/kg.K	0.6369	0.98	0.85	0.85	0.94	1.004
Heat of Combustion, MJ/kg	7.1175	3.1245	2.3729ᵇ	5.01598ᵇ	7.325	6.69
Vapor Pressure, kPa						
Solubility in Water, at 20°C, g/kg	13.2	8.22	0.8	1.40	1.07	0.95
Flash Point (ASTM), °C	none	none	none	none	none	none
Critical Temperature, °C	245.0	263.4	283.2	347.1	271.0	311.5
Critical Pressure, MPa	6.171	5.45	4.6	9.74	5.02	4.48
Critical Density, kg/m³	472	500	558	---	---	---
log Kow	no data	1.97	2.62-2.83	3.40	2.29	2.49

Sources:
Kirk-Othmer Encyclopedia of Chemical Technology, 1978
Hazardous Chemicals Desk Reference, 1987
Hazardous Substance Data Bank
ᵃ Latent heat of vaporization at bp
ᵇ Heat of combustion, liquid, at constant volume, 18.7°C
ᶜ Extrapolated or interpolated

rubber, tars, and a wide range of common organic compounds. Chloroform decomposes at ordinary temperatures in sunlight in the absence of air, and in the dark in the presence of air. Phosgene, a very toxic chemical, is one of its oxidative decomposition products. CFM resists thermal decomposition at temperatures up to about 290°C.[2]

CTC is the most unstable of the 33/50 cholormethanes under thermal oxidation, and least resistant to oxidative breakdown. The vapor decomposes and gives off toxic chemicals, such as phosgene, when in contact with a flame or very hot surface. Therefore, the commercial product frequently contains added stabilizers. CTC is miscible with many common organic liquids and is a powerful solvent for asphalt, bitumens, chlorinated rubber, ethyl cellulose, fats, gums, rosin, and waxes.[3]

PCE is the most stable of the chlorinated ethanes and ethylenes, requiring only small amounts of stabilizers. PCE dissolves sulfur, iodine, mercuric chloride, and appreciable amounts of aluminum chloride. It is a solvent for a variety of organic compounds as well as a large number of substances such as fats, oils, tars, rubber, and resins. PCE is miscible with the chlorinated organic solvents and most other common solvents. It resists hydrolysis at temperatures up to 150°C, and is stable to about 500°C in the absence of catalysts, air, and moisture. In the absence of light, PCE is unaffected by oxygen, but under ultraviolet radiation, in the presence of air or oxygen, PCE undergoes auto-oxidation to trichloroacetyl chloride.[4]

TCE is nonflammable under conditions of normal use, but exhibits a flammable range when high concentrations of vapor are mixed with air and exposed to high-energy ignition sources. In the absence of stabilizers, it is slowly auto-oxidized by air to acidic and corrosive oxidation products. Stabilizers are added to all commercial grades. TCE is miscible with many organic liquids and is a versatile solvent.[5]

TCA, also known as methyl chloroform, has a characteristic sweet, sharp odor. TCA is miscible with other chlorinated solvents and is

soluble in most common organic solvents. TCA is among the least toxic of the chlorinated solvents used in industry. It was originally developed for industrial use as a replacement for carbon tetrachloride because of its lower toxicity. The use of TCA was hampered for a number of years because of poor product stability, but the product use experienced a rapid period of growth once an adequate stabilization system was developed.[6]

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

Just as the 33/50 halogenated organic compounds have similar physical properties, they also have similar health, safety, and environmental issues associated with their production and use. All but TCA are classified as possible or probable human carcinogens by EPA. All six compounds are CNS and respiratory depressants. Exposure to all the 33/50 halogenated organic compounds except TCA is associated with liver and kidney problems.

The major routes of exposure to these compounds are through inhalation or ingestion, although dermal exposure may occur from absorption through the skin. Air emissions account for the largest environmental releases of these compounds, due to their high volatility. CTC and TCA have long atmospheric lifetimes and contribute to ozone depletion. Land disposal of these chemicals is prohibited under the Hazardous and Solid Waste Amendments of 1984. The 33/50 halogenated organic compounds are also highly mobile in soil and groundwater and are common groundwater contaminants. The particular issues associated with the 33/50 halogenated organic compounds are discussed briefly below.

Dichloromethane

Most exposure to DCM occurs via inhalation.[7] Exposure to DCM in low levels and for short durations can cause a slight irritation of the nose and throat.[8] Exposure to DCM may

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TABLE 3.2 SUPPLY AND DEMAND OF 33/50 HALOGENATED COMPOUNDS

Producer	1992 Capacity[a,b] (million lbs/yr)						Process
	CFM	DCM	CTC	PCE	TCE	TCA	
Dow Chemical, USA Freeport, TX	135	110	---	---	120	500	Chlorination of EDC (TCE) Hydrochlorination of Methanol (DCM,CFM)
Plaquemine, LA	150	120	100	90	---	---	Hydrochlorination of Methanol (DCM,CFM) Hydrocarbon Chlorinolysis (CTC, PCE)
Occidental Petroleum Corp., Belle, WV	56	111					Hydrochlorination of Methanol (CFM, DCM)
PPG Industries, Inc. Lake Charles, LA	---	---	---	200	200	350	Oxychlorination of EDC (PCE, TCE)
Vulcan Materials Geismar, LA	60	80	90	150	---	200	Hydrochlorination of Methanol (DCM, CFM) Hydrocarbon Chlorinolysis (CTC, PCE)
Wichita, KS	110	130	60	50	---	---	Hydrochlorination of Methanol and Chlorination of Methane (DCM, CFM) Hydrocarbon Chlorinolysis (CTC, PCE)
TOTAL SUPPLY	511	551	250	490	320	1,050	
1991 Demand	475	400	340	250	160	640	
1992 Demand	485	390	250	250	145	600	
1996 Demand	535	345	0[c]	350	140	0[c]	

Source:
Chemical Marketing Reporter
[a] Capacities may vary depending on product mix
[b] Akzo American/LeMoyne, AL, and Dow Chemical/Pittsburgh, CA, shut down 340 million pounds of CCl$_4$ capacity in 1991
[c] U.S. production of CCl$_4$ and TCA must be phased out by 1995

Tetrachloroethylene

Exposure to PCE may occur from its use in dry cleaning applications, as a solvent, and as an intermediate in chemical synthesis. In addition to eye and skin inflammation from contact with liquid PCE, inhalation of its vapor can cause CNS depression, liver necrosis, and effects on the lung, heart, and kidney.[23] Although PCE is not officially classified by the EPA, it is thought to be a possible-to-probable human carcinogen (Class C-B2).[24]

PCE released to the atmosphere is subject to photo-oxidation, with estimates of degradation time ranging from an approximate half-life of two months to less than one hour. If PCE is released to soil, it can evaporate into the atmosphere and leach into groundwater. If PCE is released to surface waters, it will volatilize rapidly. It is not expected to biodegrade, bioconcentrate in aquatic organisms, or readily adsorb to sediment. PCE does not significantly hydrolyze in soil or water under normal environmental conditions.[25]

Trichloroethylene

Short-term exposure to TCE has occurred through inhalation of vapors from industrial accidents, and through accidental ingestion or skin contact. TCE vapor may irritate the eyes, nose, and throat. If splashed on the skin, the liquid may cause burning, irritation, and damage. Repeated or prolonged skin contact with the liquid may cause inflammation of the skin. Short-term exposure through inhalation of TCE causes CNS depression, nausea, dizziness, headache, tremors, and confusion.[26] Acute inhalation exposure to high levels may cause coma and eventual death from liver or kidney failure.[27] Extended exposure can increase the duration and intensity of these symptoms.[28] TCE is currently being re-assessed by the EPA as to its potential to cause cancer in humans; the most recent judgement was that TCE is a possible-to-probable human carcinogen (Class C-B2).[29]

TCE enters the atmosphere from evaporation during production and use. Although most TCE is released to the air, it is also found in rivers, lakes, drinking water, soil, food, marine and freshwater biota, and humans. TCE may enter surface waters from direct releases or from the atmosphere by contaminated rainfall. TCE is not expected to persist in the open environment, but does persist in groundwater.[30] TCE is reactive in the atmosphere under smog conditions. TCE exhibits a moderate level of bioconcentration.[31]

1,1,1-Trichloroethane

TCA is less toxic than most chlorinated hydrocarbon solvents. It is, however, a CNS and respiratory depressant, as well as a mucous membrane irritant. Prolonged air exposure can result in mild eye and respiratory tract irritation. Physical contact with liquid TCA can cause skin and eye irritation. Exposure to concentrations greater than 5,000 to 10,000 ppm can be lethal. Causes of death may include respiratory and cardiac failure.[32] TCA is not classifiable as to human carcinogenicity (EPA Class D). There are no data for humans and animal studies that show evidence of carcinogenicity.[33]

TCA is likely to enter the environment from air emissions or from wastewater through its production or use. TCA is fairly stable in the atmosphere and can be transported long distances. TCA slowly degrades principally by reaction with hydroxyl radicals and has a half-life of six months to 25 years. Because of its long atmospheric half-life, TCA concentrations in the stratosphere are increasing by 12 to 17 percent/year.[34] As an ozone-depleting substance, phase-out of TCA production is mandated in the U.S. by the end of 1995.

Releases of TCA to surface water will rapidly evaporate to the atmosphere. TCA is not adsorbed strongly to soil and may leach to groundwater. Major human exposure is from air and drinking water.[35]

INDUSTRY PROFILE

Four companies at six locations in the U.S. are major producers of the 33/50 halogenated compounds. Table 3.2 lists the producers of these products, the manufacturing processes they employ, and their annual production capacities.

TABLE 3.3   PRICES OF 33/50 HALOGENATED COMPOUNDS

Chemical	Historical ($/lb)[a]		Current ($/lb)[b]
	High	Low	
CTC	0.25	0.085	0.215
CFM	0.46	0.17	0.44 to 0.46
DCM	0.32	0.07	0.29
PCE	0.31	0.095	0.29
TCA	0.64	0.09	0.64
TCE	0.45	0.105	0.45

Source:
Chemical Marketing Reporter
[a] Historical price range is from 1952 to 1994, except CTC, which is from 1952 to 1989
[b] Current price for industrial grade, bulk quantity, as of week ending January 28, 1994

co-products are also produced at one facility by the oxychlorination of ethylene dichloride (EDC). One facility uses the chlorination of EDC to produce TCE. These production processes are described below.

Hydrochlorination of Methanol

In the U.S. the predominant process of industrial production of DCM and CFM is the hydrochlorination of methanol. The process begins with the preliminary reaction of approximately equimolar ratios of hydrogen chloride and methanol, with the aid of a catalyst, to produce methyl chloride. This reaction is carried out in the vapor phase, where the two components are passed through a preheater at 180°C. The gas mixture is then passed through a converter, which is maintained at atmospheric pressure and a temperature of 340 to 350°C. The methyl chloride produced is then fed to reactors, where it is combined with chlorine to produce DCM, CFM, and CTC. Condensers are used to collect and purify the hot reaction gases. The crude CTC that is produced from this process is used as feed in the hydrocarbon chlorinolysis process to produce CTC and PCE.[43]

Direct Chlorination of Methane

Direct chlorination of methane is an irreversible process that involves directly reacting chlorine (Cl_2) with excess methane at a high temperature (approximately 485 to 510°C). Elevated temperatures are required to produce dissociation of chlorine and initiate the chlorination reaction. Methyl chloride, DCM, and CFM are the first three products of chlorination; each is subject to further chlorination to the succeeding heavier chloromethane compound. The raw material flow rates, including the initial concentration of chlorine in the feed, and the temperature, may be controlled to produce the particular chloromethane desired.

The effluent from the reactor contains unreacted methane and hydrogen chloride, which are usually separated from the chloromethanes in the scrubbing stage. The scrubber employs a refrigerated mixture of higher chloromethanes, in which the chloromethanes are only slightly soluble. The methane is freed from the acid via water scrubbing, and is recycled back to the chlorinator. The chloromethane co-products are then washed, scrubbed with alkali, dried, and passed to a sequence of fractionating columns.[44]

The ̄iected demand for these compounds, the market trends associated with their production and use, and the prices of the 33/50 halogenated chemicals are also presented below.

> *The demand for most of the 33/50 chemicals has decreased in recent years, due to concern about their health and environmental effects.*

Market Trends

Production capacity for most of the 33/50 halogenated compounds has decreased in recent years, owing to health, safety, and environmental issues. Capacity in 1992 exceeded the projected 1992 demand for each of these compounds except CTC. CTC capacity was reduced by 340 million pounds in 1991 when Akzo American in LeMoyne, Alabama and Dow Chemical in Pittsburgh, California shut down their CTC production processes.[36]

The size of the DCM market declined 3.1 percent per year from 1982 to 1991, with this negative growth expected to continue at -3.0 percent per year through 1996. Industry representatives believe that available substitutes are generally less cost-effective, but a revised permissible exposure limit proposed by OSHA could accelerate declines in some segments, particularly in paint stripper applications.[37]

CFM is the only 33/50 chlorinated organic compound for which a consistent growth of demand is projected. Historically (1982 to 1991), CFM demand has increased by 5.2 percent per year. Future growth is expected to be 2.5 percent per year.[38] Growth is projected because CFM is a feed material for hydrochlorofluorocarbon (HCFC-22) which is expected to remain a viable chlorofluorocarbon (CFC) substitute for the next decade. EPA plans to phase-out most HCFCs by 2005, with exceptions made for the servicing of existing equipment until 2015.

CTC consumption declined 0.7 percent per year between 1978 and 1988 and was projected to decline three percent per year through 1993.[39] Since the phase-out of CTC production in the

U.S. has been accelerated to 1995, the decline in consumption may be more rapid.

The demand for PCE has declined in recent years, due to its use as a feedstock for CFC-113. Market sources predict that demand should remain fairly stable through the mid 1990s, when PCE use should increase from large-scale production of CFC replacement compounds. Despite new restrictions, PCE is also expected to maintain its strong position as a solvent in the dry cleaning industry.[40]

The demand for TCE decreased an average of 1.9 percent per year between 1982 and 1991. Future demand is expected to decrease 2.6 percent per year through 1996. Use of TCE as a vapor degreaser is expected to continue its downward trend, with demand falling at the rate of two to three percent per year. If TCE becomes a potential feedstock for CFC alternatives, however, it could begin to experience renewed growth.[41]

The demand for TCA increased 0.8 percent per year between 1982 and 1991, but is expected to decrease until its phase-out at the end of 1995.[42]

Price of the 33/50 Halogenated Compounds

The price of the 33/50 halogenated compounds has fluctuated somewhat over the years. Table 3.3 presents the historical price range and current prices. Current prices for each of the compounds are at, or near, their historical highs.

PRODUCTION PROCESSES

CFM and DCM are produced as co-products by the direct chlorination of methane at one facility, and by the hydrochlorination of methanol at five facilities in the U.S. CTC is produced as a by-product of the hydrochlorination-of-methanol process at three of these facilities, and is used as feed to the hydrocarbon-chlorinolysis process. Hydrocarbon-chlorinolysis is used to produce CTC and PCE as co-products. PCE and TCE

The 33/50 halogenated organic chemicals alone contributed almost 14 percent of all TRI air emissions in 1991. The chemicals and allied products industry was the largest reported emitter of these chemicals, contributing almost 16 percent of the total.

Environmental Releases from Production

Air emissions of halogenated organic compounds from production processes can originate from the intermittent or continuous purging of inert gases from reactor vessels, drying beds, finishing columns, and other process vessels. Fugitive air emissions can result when process fluids leak from plant equipment such as pumps, compressors, and process valves. Air emissions from storage and handling operations also occur at production facilities. Other sources of environmental releases or transfers include the following:

■ wastewater discharges directly from the plant into rivers, streams or other bodies of water, or transfers to a POTW;

■ on-site release to landfills, surface impoundments, land treatment, or another mode of land disposal;

■ disposal of wastes by deep well injection; and

■ transfers of wastes to off-site facilities for treatment, storage or disposal.

The environmental releases and transfers of the 33/50 halogenated organic compounds from the major producers identified in Table 3.2 were retrieved from the 1991 TRI data. The data are presented in Table 3.4. Many of the facilities reported multiple SIC codes on one form, indicating the data may include releases from internal use of the chemicals after production.

Distribution of Environmental Releases by Industry Group

Each of the 33/50 halogenated organic chemicals, except CTC, was within the top 50 chemicals for TRI total releases and transfers in 1991. Table 3.5 lists their total releases and transfers and relative rank. TCA contributed the largest percentage of total emissions for this chemical class, accounting for 45 percent of the total releases and transfers of the 33/50 halogenated organic chemicals. Combined, the 33/50 halogenated organics accounted for almost 14 percent of all TRI air emissions in 1991.[48]

Releases and transfers of the 33/50 halogenated organics were fairly widely distributed across industry groups in 1991. Table 3.6 lists the top eight industries that emitted the largest quantities of these chemicals and their total reported releases and transfers.

The chemicals and allied products industry reported the largest total emissions of the 33/50 halogenated organics, followed by rubber and plastics products manufacturers, and the transportation industry. Releases from the chemicals and allied product result from production of the compounds and their use as chemical intermediates, as solvents, and as chemical processing aids. DCM is the halogenated organic released in the largest quantity by the chemicals and allied products industry, which includes manufacturers of plastic materials and resins. DCM is used to dissolve triacetate polymer flake to form a liquid extrudable polymer. It is also used as a solvent in the polymerization reaction to form polycarbonate resin. A major source of unintended production and release of CFM is the use of chlorine and hypochlorite to bleach virgin pulp in the paper industry. The use of chlorine and hypochlorite to remove unwanted dyes from recycled paper also generates chloroform.[49]

Hydrocarbon Chlorinolysis

Hydrocarbon chlorinolysis involves the breakage of a carbon-carbon bond when a chlorinated hydrocarbon or hydrocarbon is reacted with excess chlorine at a high temperature, usually 400 to 700°C. Since fully-chlorinated hydrocarbons, with fewer carbon atoms than the starting material, are obtained, the process is frequently referred to as perchlorination.

Propane, propylene, acetylene, naphthalene, ethylene dichloride, and crude CTC are used as feedstocks in the hydrocarbon-chlorinolysis process. The hydrocarbon feed, fresh Cl_2, and recycled Cl_2 are fed to a vaporizer, where they are mixed with recycled chlorides. The mixed gases are then fed to a refractor-lined reactor, which operates at high temperatures and at atmospheric pressure. After startup, the reaction is self-sustaining. The CTC/PCE ratio is controlled by the diluent action of the recycled chlorides. Effluent from the reactor consists mainly of CTC, PCE, hydrogen chloride (HCl), and excess chlorine, along with unreacted hydrocarbons. The hot effluent gas is quenched and HCl and Cl_2 are removed. The liquid stream from the quenched gas is separated into CTC and PCE by distillation. Heavy ends from the distillation column are recycled back to the feed tank.[45]

Chlorination of Ethylene Dichloride

Dow Chemical in Freeport, Texas, uses the chlorination of EDC to produce TCE. EDC is first produced by the chlorination of ethylene. The EDC is further chlorinated in an exothermic reaction carried out in the presence of a catalyst at 280 to 450°C. Temperature in the reactor is controlled by a fluidized bed, a molten salt bath, or the addition of an inert material. PCE can also be produced by the chlorination of EDC as a co-product by varying reaction conditions.

Oxychlorination of Ethylene Dichloride

PPG Industries employs the oxychlorination of EDC to produce both PCE and TCE. The product mix can be varied by adjusting the mole-feed ratios of EDC, Cl_2, and oxygen. The single-stage reaction occurs in the presence of a catalyst, at a temperature around 430°C, and a pressure slightly above one atmosphere. The build-up of a great amount of hydrogen chloride is avoided by concomitantly operating HCl oxidation. The reaction involves the simultaneous oxychlorination/ dehydrochlorination using chlorine or anhydrous hydrogen chloride as the chlorine source.[46]

Production of TCA

The most widely used process for producing TCA involves the dehydrochlorination of EDC to vinyl chloride, which is then hydrochlorinated to 1,1-dichloroethane. The 1,1-dichloroethane is thermally or photochemically chlorinated to produce TCA. In another important process, hydrogen chloride is added to 1,1-dichloroethylene in the presence of an iron chloride catalyst to produce TCA.

When vinyl chloride is used, a preparatory step must be performed to break the double bond while maintaining all the chlorine atoms on one carbon. This is usually accomplished through hydrochlorination, using hydrogen chloride. Hydrochlorination can also be used with a vinylidene-chloride feed, which results in the direct production of TCA. Typical reaction temperatures for the thermal chlorination range from 370 to 430°C. This is a highly exothermic reaction, with much of the liberated energy being taken out as sensible heat along with the products.[47]

ENVIRONMENTAL RELEASES OF 33/50 HALOGENATED COMPOUNDS

Environmental releases of the 33/50 halogenated organics occur from their production, use, and disposal. The discussion below presents the types of releases and transfers that occur from production facilities, the releases and transfers reported by the major producers of these chemicals in the 1991 TRI, and the distribution of environmental releases by industry group.

TABLE 3.4 (CONTINUED)

Producer	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Occidental Petroleum, Belle, WV								
CFM	26,459	236	0	0	26,695	1	624	625
DCM	68,066	245	0	0	68,311	1	1,030	1031
TOTAL	94,525	481	0	0	95,006	2	1,654	1,656
PPG Industries, Westlake, LA								
PCE	154,627	2,418	0	0	157,045	N/A	363,260	363,260
TCE	169,424	1,435	0	0	170,859	N/A	50,496	50,496
TCA	132,517	984	4	0	133,505	N/A	25,550	25,550
TOTAL	456,568	4,837	4	0	461,409	0	439,306	439,306
Vulcan Materials, Geismar, LA								
CFM	61,590	226	0	0	61,816	N/A	3,150	3,150
DCM	64,800	38	0	0	64,838	N/A	2,150	2,150
CTC	74,670	22	0	0	74,692	N/A	5,050	5,050
PCE	55,600	16	0	0	55,616	N/A	3,300	3,300
TCA	95,600	16	0	0	95,616	N/A	2,000	2,000
TOTAL	352,260	318	0	0	352,578	0	15,650	15,650
Vulcan Chemicals, Wichita, KS								
CFM	301,800	0	0	65,000	366,800	N/A	733	733
DCM	54,700	0	0	25,000	79,700	N/A	72	72
CTC	144,200	0	0	42,000	186,200	N/A	921	921
PCE	88,400	0	0	14,000	102,400	N/A	469	469
TOTAL	589,100	0	0	146,000	735,100	0	2,195	2,195

Source:
TRI, 1991
N/A: Not Available

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TABLE 3.4 RELEASES AND TRANSFERS OF 33/50 HALOGENATED COMPOUNDS FROM PRODUCTION FACILITIES

Producer	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Akzo, Axis, AL								
CTC	100,000	1,100	0	0	101,100	N/A	23	23
Dow Chemical, Freeport, TX								
PCE	29,000	240	0	0	29,240	0	34,100	34,100
CFM	86,000	1,200	0	0	87,200	N/A	0	0
DCM	155,000	460	0	0	155,460	N/A	0	0
TCE	18,100	13	0	0	18,113	N/A	0	0
TCA	176,000	2	0	0	176,002	0	0	0
TOTAL	464,100	1,915	0	0	466,015	0	34,100	34,100
Dow Chemical, Pittsburgh, CA								
CTC	11,600	7	0	0	11,607	N/A	6,300	6,300
DCM	29,000	2	0	0	29,002	N/A	111,100	111,100
PCE	17,900	5	0	0	17,905	N/A	6,500	6,500
TCE	780	0	0	0	780	N/A	400	400
TOTAL	59,280	14	0	0	59,294	0	124,300	124,300
Dow Chemical, Plaquemine, LA								
CFM	74,000	860	0	0	74,860	N/A	49	49
DCM	143,000	20	0	0	143,020	N/A	28	28
CTC	41,000	260	2,000	0	43,260	0	14	14
PCE	18,900	200	252	0	19,352	N/A	600	600
TOTAL	276,900	1,340	2,252	0	280,492	0	691	691

TABLE 3.6 TOP INDUSTRIES FOR TOTAL TRI RELEASES AND TRANSFERS OF 33/50 HALOGENATED ORGANIC COMPOUNDS

Chemical	Releases and Transfers (lbs/yr)[a]							
	Paper SIC 26 (lbs)	Chemicals SIC 28 (lbs)	Plastics SIC 30[b] (lbs)	Primary Metals SIC 33 (lbs)	Fabricated Metals SIC 34 (lbs)	Electrical SIC 36 (lbs)	Transport. SIC 37 (lbs)	Multiple Code SIC 20-39 (lbs)
CFM	17,766,992	3,421,843	3,100	0	0	0	0	1,315,756
CTC	18	2,390,894	2,024	6,493	0	0	70,500	51,862
DCM	90,730	34,502,790	24,585,522	1,541,356	2,593,162	3,283,759	4,076,263	8,661,283
PCE	55,949	2,023,479	586,562	1,477,874	2,839,051	3,543,450	3,398,197	3,366,421
TCA	1,398,280	7,442,763	20,457,040	15,252,550	17,792,087	13,690,513	26,605,782	13,790,547
TCE	100,399	1,939,657	1,465,747	2,840,240	10,297,752	4,138,793	4,529,113	5,235,960
TOTAL RELEASES AND TRANSFERS	19,412,368	51,721,426	47,099,995	21,118,513	33,522,052	24,656,515	38,679,855	32,421,829
PERCENT OF TOTAL RELEASES AND TRANSFERS[c]	5.98	15.93	14.50	6.50	10.32	7.59	11.91	9.98

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office
[a] Based on 1991 data
[b] Rubber and plastic manufacturers
[c] Total for all 33/50 halogenated organics for all industry groups in 1991 was 324,732,979 lbs.

TABLE 3.5   TOTAL RELEASES AND TRANSFERS OF 33/50 HALOGENATED ORGANIC COMPOUNDS

Chemical	Releases and Transfers (lbs/yr)	TRI Rank
CTC	2,575,457	73
CFM	22,576,422	36
DCM	94,786,380	14
PCE	20,797,397	38
TCA	145,996,101	10
TCE	38,001,222	26
TOTAL	324,732,979	

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

USES OF THE HALOGENATED ORGANIC COMPOUNDS

The six 33/50 halogenated organic chemicals are widely used as cleaning solvents, as chemical intermediates in the manufacture of fluorocarbons and other chemicals, and as components of consumer products. The uses are illustrated in a chemical-use tree diagram shown on Figure 3.1.[50]

> *Three use clusters of the 33/50 halogenated organic chemicals were selected for substitutes evaluation: metal and parts degreasing, dry cleaning, and paint stripping. Not only do these use clusters represent three of the largest uses of the 33/50 halogenated organics, they also represent applications where there is significant risk of release or exposure.*

To illustrate the potential for the increase in production of one compound as the use of another decreases, the chemical-use tree diagram

also shows production processes and co-products. For example, CTC production has dropped significantly since the chlorofluorocarbon restrictions took effect, causing those who co-produce CTC and PCE to swing their production to PCE.[51]

The numbers along each branch of the chemical-use tree are weight fractions of the usage of the chemical or product in the first box to produce the chemical or product in the second box. For example, in Figure 3.1, 98 percent of the chloroform produced is used to manufacture fluorocarbon-22; 70 percent of the fluorocarbon-22 produced is used as refrigerants. Where there is a box that is divided, the chemicals or products are co-products. For example, CFM and DCM are co-products of methanol hydrochlorination.

Metal and parts degreasing, dry cleaning, and paint stripping applications of the 33/50 halogenated organic compounds have been selected as priority use clusters for substitutes evaluation. These use clusters were selected based on the following criteria: 1) the relative magnitude of the product or use; 2) the status of the product or use (products with a federally

mandated phase-out schedule were not selected); and 3) the qualitative risk of release or exposure from the product or use. These priority use clusters, and some of the other major products and uses of the chlorinated solvents, are discussed briefly below.

Fluorocarbon Production

The largest single use of the 33/50 halogenated organic compounds is as a precursor for the manufacture of CFCs and HCFCs. CTC, CFM, and PCE are all used as chemical intermediates in the production of CFCs (Fluorocarbons-11, -12 and -113) and HCFCs (Fluorocarbon-22). Based on the chemical-use tree diagram and the 1991 demand data, this use consumed approximately 845 million pounds of 33/50 halogenated organic compounds, or roughly 37 percent of these chemicals consumed that year. TCE is also being evaluated as a precursor in the production of CFC replacement compounds, such as HFC-134a and HCFC-123.

Although the production of CFCs and HCFCs is the most significant use in terms of mass, this use was not selected for substitute evaluation, since these compounds are scheduled for phase-out, and significant progress has been made in identifying and implementing effective substitutes. The Montreal Protocol and the Clean Air Act Amendments of 1990 calls for a phase-out of CTC and ozone-depleting CFCs by the year 2000, and the elimination of HCFCs by 2030. The U.S. has accelerated this phase-out schedule and ordered CTC and CFC manufacturers to halt production by the end of 1995. In addition, EPA proposes phasing-out the HCFCs with the highest depletion potential by 2005, with exceptions made for the servicing of equipment until 2015.

Metal and Parts Degreasing

Based on the chemical-use tree and 1991 demand data, approximately 535 million pounds of the 33/50 halogenated organics, including DCM, PCE, TCE, and TCA were consumed in metal and parts degreasing applications in 1991.

This represents approximately 24 percent of the total consumed that year, indicating that metal cleaning is the second largest use by weight of these chemicals.

Chlorinated solvents have been popular industrial solvents since they were first produced. However, in recent years, with the increased awareness of the health, safety, and environmental issues surrounding their use, alternatives to chlorinated-solvent metal cleaning have been identified. Several viable alternatives exist, and substantial progress is being made in pollution prevention in metal and parts cleaning by use of safe substitutes. Safe substitutes for 33/50 halogenated compounds used in degreasing applications are evaluated in Chapter 9.

Dry Cleaning

Both PCE and TCA are used to dry clean fabrics, although TCA use represents only a small fraction of the 33/50 halogenated organic compounds consumed in dry cleaning operations. PCE is the solvent of choice in the U.S. for dry cleaning fabrics, evidenced by its market share for this process (more than 75 percent). The effects of dry cleaning on the environment are evidenced by increased concentrations of PCE in ambient air in urban areas. Alternatives to the dry cleaning process and safe substitute dry cleaning solvents are evaluated in Chapter 10.

Consumer Products

DCM and TCA are used in consumer products such as paint stripping formulations and aerosols. Paint stripping and aerosol applications of these two chemicals account for 12 percent of their use. Two of the significant features of these applications are the following: 1) all DCM and TCA consumed in these products are released to the environment, primarily through volatilization; and 2) consumers are exposed to the chemicals during the application and use of the products.

DCM and TCA use in aerosols has decreased in recent years, as different propellants, such as carbon dioxide, have come into prevalent use.
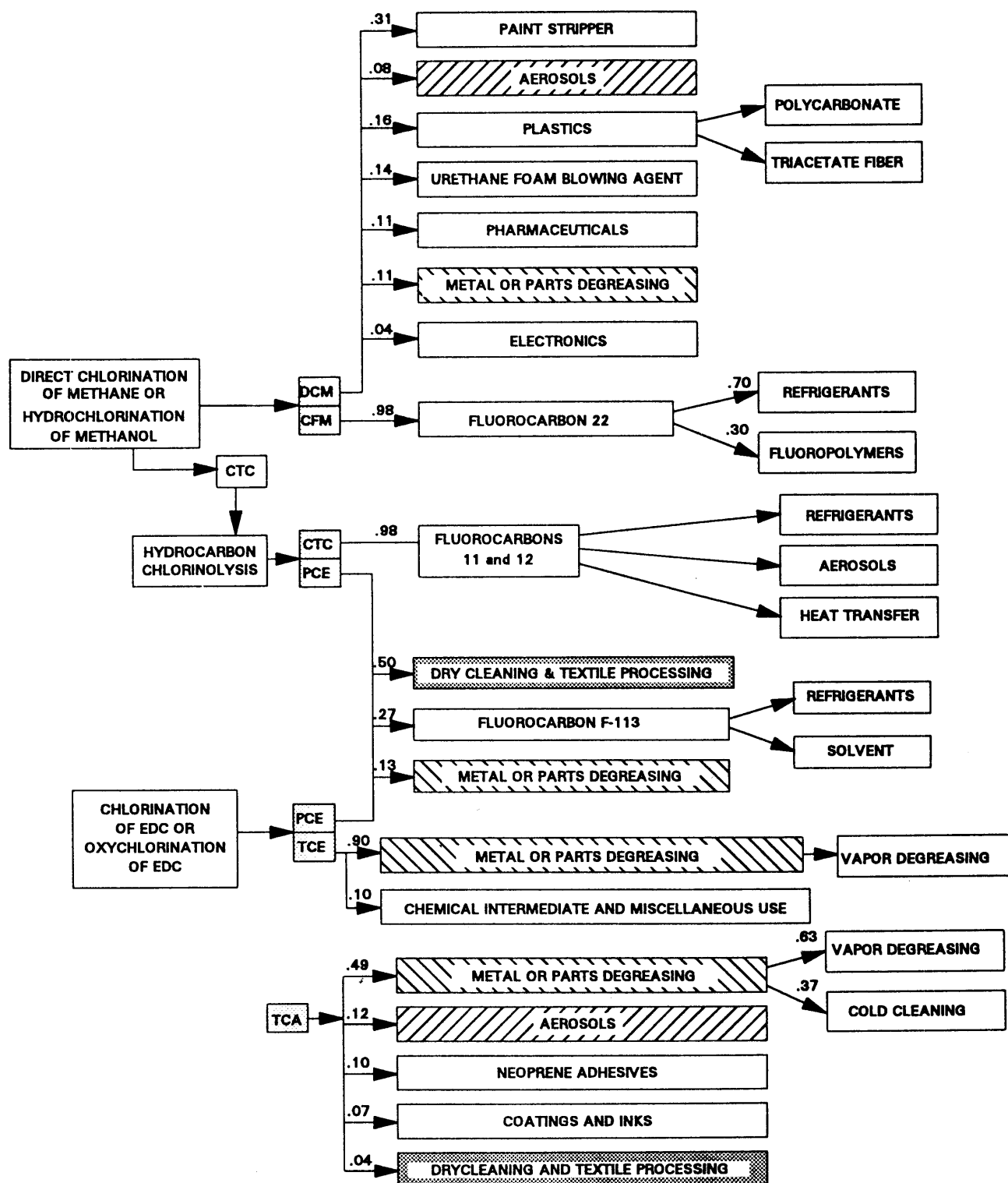
FIGURE 3.1   CHLORINATED ORGANICS

NOTE: Shaded regions identify use clusters associated with the halogenated organic chemicals
        Reliable data were not available to estimate weight fractions along some branches of the chemical-use tree

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ENDNOTES

[1] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., (New York: John Wiley, 1993), Vol. 5.

[2] Ibid.

[3] Ibid.

[4] Ibid.

[5] Ibid.

[6] Ibid.

[7] International Programme on Chemical Safety, Methylene Chloride, Environmental Health Criteria 32, (Geneva World Health Organization, 1990).

[8] Hampshire Research Associates, Inc., *Toxics in the Community*, US EPA, Office of Toxic Substances, Economic and Technology Division, (Washington: GPO, 1989).

[9] International Programme on Chemical Safety, Methylene Chloride, Environmental Health Criteria 32, (Geneva World Health Organization, 1990).

[10] Hampshire Research Associates, Inc., *Toxics in the Community*, US EPA, Office of Toxic Substances, Economic and Technology Division, (Washington: GPO, 1989).

[11] "Dichloromethane," *Integrated Risk Management System*, 1994.

[12] International Programme on Chemical Safety, Methylene Chloride, Environmental Health Criteria 32, (Geneva World Health Organization, 1990).

[13] Ibid.

[14] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., (New York: John Wiley, 1993), Vol. 5.

[15] "Chloroform," *Hazardous Substances Data Bank*, August 23, 1990.

[16] "Chloroform," *Integrated Risk Information System*, 1994.

[17] "Chloroform," *Hazardous Substances Data Bank*, August 23, 1990.

[18] Ibid.

[19] *Carbon Tetrachloride: Chemical Information Sheet*, Illinois Environmental Protection Agency, Office of Chemical Safety, February 1989.

[20] "Carbon Tetrachloride," *Integrated Risk Information System*, 1994.

Also, use of TCA in general is declining, because producers are anticipating the phase-out of this chemical as an ozone-depleting substance.

New paint stripping methods, such as blasting methods, heat technologies, and alkaline or acid strippers, are beginning to replace DCM-based paint strippers in industrial applications. Alternative chemical formulations are beginning to be employed in certain applications in the consumer market. Chapter 11 presents an evaluation of safe substitutes for DCM-based paint strippers.

[44] Ibid.

[45] *Survey of Carbon Tetrachloride Emission Sources*, US EPA, Pub. No. EPA 450/3-85-018, (Research Triangle Park, NC, July 1985).

[46] *Survey of Perchloroethylene Emission Sources*, US EPA, (Research Triangle Park, NC, July 1985).

[47] *Encyclopedia of Chemical Processing and Design*, Vol. 8.

[48] *1991 Toxics Release Inventory, Public Data Release*, US EPA, Office of Pollution Prevention and Toxics, May 1993.

[49] Timothy E. McKinney, "Alternative Chemicals Gain Popularity for Bleaching of Woodfree Furnishes," *Pulp and Paper*, March 1992.

[50] Sources for Figure 3.1:
"Chemical Profile: Methylene Chloride," *Chemical Marketing Reporter*, March 2, 1992.
"Chemical Profile: Chloroform," *Chemical Marketing Reporter*, February 24, 1992.
"Chemical Profile: Carbon Tetrachloride," *Chemical Marketing Reporter*, February 17, 1992.
"Chemical Profile: 1,1,1-Trichloroethane," *Chemical Marketing Reporter*, January 27, 1992.
"Chemical Profile: Trichloroethylene," *Chemical Marketing Reporter*, February 3, 1992.
"Chemical Profile: Perchloroethylene," *Chemical Marketing Reporter*, January 20, 1992.
Ralph C. Downing, *Fluorocarbon Refrigerants Handbook*, (Englewood Cliffs, NJ: Prentice Hall, 1988).
Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed., (New York: John Wiley, 1993), Vol. 5.

[51] "Chemical Profile: Perchloroethylene," *Chemical Marketing Reporter*, January 10, 1992.

[21] *Carbon Tetrachloride: Chemical Information Sheet*, Illinois Environmental Protection Agency, Office of Chemical Safety, February 1989.

[22] Ibid.

[23] "Tetrachloroethylene," *Hazardous Substances Data Bank*, October 23, 1990.

[24] Superfund Health Risk Technical Support Center, April 1994.

[25] "Tetrachloroethylene," *Hazardous Substances Data Bank*, October 23, 1990.

[26] *Trichloroethylene: Chemical Information Sheet*, Illinois Environmental Protection Agency, December 1986.

[27] "Trichloroethylene," *Hazardous Substances Data Bank*, 1994.

[28] *Trichloroethylene: Chemical Information Sheet*, Illinois Environmental Protection Agency, December 1986.

[29] Superfund Health Risk Technical Support Center, April 1994.

[30] *Trichloroethylene: Chemical Information Sheet*, Illinois Environmental Protection Agency, December 1986.

[31] "Trichloroethylene," *Hazardous Substances Data Bank*, 1994.

[32] "1,1,1 - Trichloroethane," *Hazardous Substances Data Bank*, October 22, 1990.

[33] "1,1,1 - Trichloroethane," *Integrated Risk Information System*, 1994.

[34] "1,1,1 - Trichloroethane," *Hazardous Substances Data Bank*, October 22, 1990.

[35] Ibid.

[36] "Chemical Profile: Carbon Tetrachloride," *Chemical Marketing Reporter*, February 17, 1992.

[37] "Chemical Profile: Methylene Chloride," *Chemical Marketing Reporter*, March 2, 1992.

[38] "Chemical Profile: Chloroform," *Chemical Marketing Reporter*, February 24, 1992.

[39] "Chemical Profile: Carbon Tetrachloride," *Chemical Marketing Reporter*, February 17, 1992.

[40] "Chemical Profile: Perchloroethylene," *Chemical Marketing Reporter*, January 20, 1992.

[41] "Chemical Profile: Trichloroethylene," *Chemical Marketing Reporter*, February 3, 1992.

[42] "Chemical Profile: Trichloroethane," *Chemical Marketing Reporter*, January 27, 1992.

[43] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., (New York: John Wiley, 1993), Vol. 5.

TABLE 4.1   SELECTED PROPERTIES OF HYDROGEN CYANIDE AND SODIUM CYANIDE

Property	Hydrogen Cyanide	Sodium Cyanide
Chemical formula	HCN	NaCN
CAS No.	74-90-8	143-33-9
Molecular Weight	27.03	49.02
Boiling Point, at 101.3 kPa, °C	25.7	1500
Melting Point, °C	-13.24	+563.7
Specific Gravity, at 20°C	0.829[a]	1.60
Viscosity, at 30°C, cP	0.2014[b]	4
Heat of Vaporization, at 101.3 kPa, kJ/mol	25.20	156.37
Heat of Capacity, at 25°C, kJ/kgK	2.63	1.402
Heat of Fusion, kJ/kg	310	314
Vapor Pressure, at 20°C, kPa	83	0.4452[c]
Flash point, °C	-17.8	N/A
Critical temperature, °C	183.5	N/A
Critical pressure, MPa	5	N/A

Sources:
Kirk-Othmer Encyclopedia of Chemical Technology, 3rd ed.
Ullmann's Encyclopedia of Industrial Chemistry, 5th ed.
[a] for 60.237 percent HCN
[b] at 20.2°C
[c] Vapor Pressure at 900°C
N/A: Not Available

metabolic system and causing rapid death. Within seconds to minutes of inhalation or ingestion of cyanide, symptoms such as giddiness, abnormally rapid or deep breathing, shortness of breath, headache, palpitation, cyanosis, and unconsciousness occur. Overexposure may produce sudden loss of consciousness, convulsions, and prompt death from respiratory arrest. It is also possible for cyanide to cause blindness and damage to optic nerves and the retina.[4]

> *The 33/50 cyanide compounds are acutely poisonous, interfering with the metabolic system and causing rapid death. Major sources of cyanide releases to the environment are the metal finishing industries, iron and steel mills, organic chemical industries, and vehicle exhaust.*

Major sources of cyanide releases to water include the metal finishing industries, iron and steel mills, and organic chemical industries. Vehicle exhaust releases cyanide to the air. The primary releases to the soil appear to be from cyanide-containing waste landfills and the use of cyanide-containing road salts. In water and soil the fate of cyanide is predicted to be pH-dependent. It may occur in the form of hydrogen cyanide, alkali metal salts, or immobile metallocyanide complexes. In subsurface soils, low concentrations of cyanide will probably biodegrade. Cyanide may also leach into groundwater. Bacteria and protozoa may degrade cyanide by converting it to carbon dioxide and ammonia. Cyanide is converted to cyanate during chlorination of water supplies.[5]

Most cyanide in the atmosphere exists as hydrogen cyanide gas, but small amounts of metal cyanides may be present as particulate matter. Hydrogen cyanide reacts with

CHAPTER 4

HYDROGEN CYANIDE AND CYANIDE COMPOUNDS

Hydrogen cyanide and cyanide compounds are the fourth class of chemicals included in EPA's 33/50 Program. The 33/50 cyanide compounds are those where a formal dissociation of the compounds may occur to yield the cyanide moiety CN^-.[1] Cyanide compounds are reported in the 1991 TRI under the aggregate heading of "cyanide compounds," except hydrogen cyanide, which is reported separately.

Cyanides are produced by industry in many different forms. Sodium cyanide and hydrogen cyanide are the two most common industrial cyanide compounds and are discussed in the most detail in this section.

PHYSICAL PROPERTIES

Selected physical properties and the chemical formulae of hydrogen cyanide and sodium cyanide are shown in Table 4.1. The physical characteristics are summarized below.

Hydrogen cyanide (HCN) is a liquid below 26.5°C, with a characteristic odor of bitter almonds. It is a very weak acid compound that is miscible with water and alcohol but only slightly soluble in ether.[2] It is normally not considered corrosive, but will corrode steel under certain conditions. Hydrogen cyanide burns with a very hot flame in the presence of oxygen or air.

Sodium cyanide (NaCN) is an alkali-metal cyanide. It is a colorless, hygroscopic salt that has a slight odor of hydrogen cyanide (bitter almonds) and ammonia in moist air. It is a white crystalline solid at room temperature. In the absence of air, carbon dioxide, and moisture sodium cyanide is stable at fairly high temperature and can be stored indefinitely. It is fairly soluble in water where it will form sodium salt hydrates. Sodium cyanide is totally decomposed to hydrogen cyanide by the actions of strong acids. Molten sodium cyanide reacts violently with strong oxidizing agents such as nitrates and sodium cyanide chlorates.[3]

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

Exposure to cyanides can occur by inhalation, ingestion, or absorption through skin and mucosal surfaces. Cyanides, such as hydrogen cyanide, potassium cyanide, and sodium cyanide, are acutely poisonous, interfering with the

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TABLE 4.3   SODIUM CYANIDE PRODUCTION CAPACITY

Producer	Location	Capacity (million lbs/yr)
Cyanco Co./Alta Gold	Winnemuca, NV	30
Degussa Corp.	Mobile, AL	60
Du Pont Co.	Memphis, TN	250
Du Pont Co.	Texas City, TX	100
FMC Corp.	Green River, WY	60
Sterling Chemical	Texas City, TX	N/A
TOTAL		500

Sources:

Capacity: *Chemical Marketing Reporter*, February 11, 1991
Companies: *1992 Directory of Chemical Producers: United States of America*, SRI International
N/A: Not Available

cyanide plants or increase their capacities because gold prices were high. When the price of gold subsequently dropped from $450 per ounce in 1988 to $366 per ounce in February of 1991, the world-wide sodium cyanide market was depressed by oversupply and slowing growth. Projections are for continued overcapacity for several years; operating rates are predicted to be at 55 to 70 percent capacity.[10]

Price of Cyanide Compounds

Table 4.4 presents the historical price range of hydrogen cyanide and the current prices for both hydrogen cyanide and sodium cyanide. The price of hydrogen cyanide is at its historical high. The price of sodium cyanide has decreased in recent years due to oversupply and slowing growth.

PRODUCTION PROCESSES

Hydrogen cyanide is produced commercially by the Andrussow process. Sodium cyanide is manufactured from hydrogen cyanide by the neutralization process. These processes are discussed below.

Production of Hydrogen Cyanide

The Andrussow process has been the most widely used process for producing hydrogen cyanide since its introduction in 1964. Here, methane, ammonia, and air (oxygen) are reacted over a platinum catalyst at 1,000 to 1,200°C. The reaction is extremely rapid, but the pathway to formation of hydrogen cyanide is not direct. Because the hydrogen cyanide will tend to polymerize under high pH conditions, sulfuric acid is added to the process to maintain a low pH. Various absorption and distillation steps are utilized in order to process the various streams for recovery of ammonia reagent.

A disadvantage of this process is that the offgas stream from the reactor contains dilute hydrogen cyanide gas. Therefore, recovery equipment must be large enough to process large volumes of gas. Also, the unreacted ammonia concentration is great enough that it must be recycled or recovered. Positive aspects of the process include the fact that the raw materials are relatively cheap, and the overall catalyst costs are low.[11] Hydrogen cyanide is also produced as a by-product of the ammoxidation of propylene during the production of vinyl cyanide.[12]

photochemically generated hydroxyl radicals at a very slow rate with a half-life of approximately 334 days. It is also expected to be resistant to direct photolysis. Because of this slow rate of degradation, hydrogen cyanide has the potential to be transported over long distances before being removed by physical or chemical processes.[6] Cyanide, however, is not accumulated or stored in any mammalian species, and hydrogen cyanide is not strongly partitioned into the sediments or suspended adsorbents, due to its high solubility in water.[7]

INDUSTRY PROFILE

Hydrogen cyanide is produced by nine companies at 13 locations in the U.S. Sodium cyanide can be produced by four companies at five locations. Tables 4.2 and 4.3 identify the current producers and production capacities of hydrogen cyanide and sodium cyanide, respectively. The market trends associated with

the production and use of the 33/50 cyanide compounds and their prices are presented below.

Market Trends

The projected growth rate for hydrogen cyanide is three to four percent per year through 1997. Hydrogen cyanide is seeing an increased demand because of strong demand for nylon and methyl methacrylate (MMA), two products manufactured using hydrogen cyanide. In 1990, market sources indicated that production of the hydrogen cyanide end products, particularly MMA, was limited because the hydrogen cyanide capacity had not kept up with the demand.[8] Conversely, increasing uses of water-borne lacquer systems is expected to decrease the demand for MMA-based acrylic lacquers, thus decreasing the demand for HCN.[9]

One of the major uses of sodium cyanide is to leach gold from its ore. Since high gold prices make it more economically feasible to mine gold, the demand for sodium cyanide is closely linked to the price of gold. In the mid to late 1980s, manufacturers made plans to open new sodium

TABLE 4.2   HYDROGEN CYANIDE PRODUCTION CAPACITY

Producer	Location	Capacity (million lbs/yr)
American Cyanamid Co.	Westwego, LA	60
BP Chemicals, Inc.	Port Lavaca, TX	70
BP Chemicals, Inc.	Lima, OH	35
Ciba-Geigy	St. Gabriel, LA	90
Degussa/Du Pont Co.	Theodore, AL	55
Dow Chemical U.S.A.	Freeport, TX	20
Du Pont Co.	Beaumont, TX	60
Du Pont Co.	Memphis, TN	200
Du Pont Co.	Orange, TX	320
Du Pont Co.	Victoria, TX	300
Monsanto Co.	Alvin, TX	60
Rohm and Haas Co.	Deer Park, TX	200
Sterling Chemicals, Inc.	Texas City, TX	90
TOTAL		1,560

Source:
Chemical Marketing Reporter, May 24, 1993

TABLE 4.5 RELEASES AND TRANSFERS OF HYDROGEN CYANIDE AND SODIUM CYANIDE FROM PRODUCTION FACILITIES

Producer	Releases and Transfers (lbs/yr)							
Hydrogen Cyanide	Air Release	Water Release	Land Release	Underground Injection Release	Total Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
American Cyanamid, Westwego, LA	2,620	0	0	0	2,620	N/A	0	0
BP Chemicals, Port Lavaca, TX	34,400	0	0	0	34,400	N/A	0	0
BP Chemicals, Lima, OH	11,700	250	0	0	11,950	N/A	0	0
Ciba-Geigy, St. Gabriel, LA	267	237	0	0	504	N/A	24	24
Degussa/Du Pont, Theodore, AL	2,460	0	0	0	2,460	0	4	4
Dow Chemical, Freeport, TX	4	0	0	0	4	N/A	0	0
Du Pont, Beaumont, TX	6,300	0	0	0	6,300	N/A	0	0
Du Pont, Memphis, TN	30,171	0	0	0	30,171	N/A	0	0
Du Pont, Orange, TX	70,498	N/A	0	412,964	483,462	N/A	N/A	0
Du Pont, Victoria, TX	7,870	0	17	142,880	150,767	0	39	39
Monsanto, Alvin, TX	2,900	0	0	390,000	392,900	0	N/A	0
Rohm and Haas, Deer Park, TX	110,560	0	0	0	110,560	N/A	0	0
Sterling Chemicals, Texas City, TX	47,160	0	0	0	47,160	N/A	N/A	0
TOTAL	326,910	487	17	945,844	1,273,258	0	67	67
Sodium Cyanide[a]								
Du Pont, Memphis, TN	3,053	0	0	0	3,053	1,069	N/A	1,069
Cyanco, Winnemuca, NV	23	0	0	0	23	N/A	0	0
Degussa, Freeport, TX	67,000	0	0	0	67,000	N/A	0	0
Sterling Chemicals, Texas City, TX	0	0	0	132,700	132,700	150	2,440	2,590
TOTAL	70,076	0	0	132,700	202,776	1,219	2,440	3,659

Source: TRI, 1991
[a] Reported as production of cyanide compounds; sodium cyanide was not reported separately in the 1991 TRI
NA: Not Available

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TABLE 4.4   PRICES OF HYDROGEN CYANIDE AND SODIUM CYANIDE

Chemical	Historical Price ($/lb)[a]		Current Price ($/lb)[b]
	High	Low	
Hydrogen Cyanide	0.60	0.115	0.60
Sodium Cyanide	N/A	N/A	0.60

Source:
Chemical Marketing Reporter
[a] Historical price range is from 1957 to 1990
[b] Current price for industrial grade, bulk quantity, as of week ending February 7, 1994
N/A: Not Available

Production of Sodium Cyanide

The manufacture of sodium cyanide is known as the neutralization process or wet process. Here, purified anhydrous liquid hydrogen cyanide (hydrocyanic acid), sometimes in vapor form, is reacted with 50 percent sodium hydroxide solution (caustic soda). The utmost purity of the reactants in turn yields 99 percent sodium cyanide.[13]

Large commercial plants use purified hydrogen cyanide from the Andrussow process to manufacture sodium cyanide. The downstream processing steps after the neutralization step include evaporation, for removal of water, and crystallization. As in the hydrogen cyanide process, it is crucial to avoid the polymerization of the hydrogen cyanide reagent, which can occur under high pH conditions.

The neutralization process is not energy intensive except for the heat needed to evaporate the water in the sodium hydroxide solution and formed in the reaction. Waste from the process contains 10 to 100 ppm of sodium cyanide and must be treated.

ENVIRONMENTAL RELEASES FROM PRODUCTION

Environmental releases of the 33/50 cyanide compounds occur from their production, use, and disposal. The types of releases and transfers that may occur from production facilities, the releases and transfers reported by the major producers of these chemicals in the 1991 TRI, and the distribution of environmental releases by industry group are presented below.

> *In 1991, the chemicals and allied products industry contributed almost 78 percent of the total reported releases and transfers of both hydrogen cyanide and cyanide compounds. In this industry, releases occur from the manufacture of cyanides and from their use as chemical intermediates in the production of plastics and resins and other chemical products. Electroplating, another use of cyanide compounds, and plastics and reins were selected for substitutes evaluation.*

Environmental Releases from Production Facilities

The environmental releases and transfers of the 33/50 cyanide compounds from the major producers identified in Tables 4.2 and 4.3 were retrieved from the 1991 TRI data. The data are presented in Table 4.5. Some of the facilities reported multiple SIC codes on one form, indicating the data may include releases from internal use of the chemicals after production. Facilities that use hydrogen cyanide as a chemical intermediate often produce their own

TABLE 4.6   TOTAL RELEASES AND TRANSFERS OF 33/50 CYANIDES

Chemical	Releases and Transfers (lbs/yr)	TRI Rank
Cyanide Compounds Hydrogen Cyanide	5,635,763 2,210,281	53*
TOTAL	7,846,044	

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office
* TRI rank for hydrogen cyanide and cyanide compounds combined

TABLE 4.7   TOP INDUSTRIES FOR TOTAL TRI RELEASES AND TRANSFERS OF 33/50 CYANIDES

Chemical	Releases and Transfers (lbs/yr)[a]			
	Chemicals SIC 28	Primary Metals SIC 33	Fabricated Metals SIC 34	Multiple Code SIC 20-39
Cyanide Compounds Hydrogen Cyanide	4,120,654 1,967,177	717,896 475	415,031 0	281,953 49,937
TOTAL RELEASES AND TRANSFERS	6,087,831	718,371	415,031	331,890
PERCENT OF TOTAL RELEASES AND TRANSFERS[b]	77.59	9.16	5.29	4.23

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office
[a] Based on 1991 data
[b] Total for all 33/50 cyanides for all industry groups in 1991 was 7,846,044 lbs.

Metal finishing includes electroplating and other processes to increase the corrosion resistance, hardness, aesthetic value or other properties of a product. The 33/50 metals and sodium cyanide are widely used in electroplating.

As discussed in Chapter 1, electroplating was selected for substitutes evaluation because of the potential benefits of identifying safe substitutes that would reduce the use of chemicals in two of the 33/50 chemical classes.

hydrogen cyanide on-site because of the hazards posed by shipping and handling the poisonous gas.

Air emissions contributed the largest fraction of total releases and transfers reported by cyanide compound production facilities. Process air emissions from production processes can originate from the continuous or intermittent purging of inert gases from reactor vessels, drying beds, finishing columns, and other process vessels. Fugitive air emissions result when process fluid leaks from plant equipment such as pumps, compressors and process valves. Air emissions from storage and handling operations also occur at production facilities.

Other sources of environmental releases or transfers include the following:

- wastewater discharges directly from the plant into rivers, streams, or other bodies of water, or transfers to a POTW;

- on-site release to landfills, surface impoundments, land treatment or another mode of land disposal; and

- transfers of wastes to off-site facilities for treatment, storage, or disposal.

Distribution of Environmental Releases by Industry Group

Table 4.6 lists the total releases and transfers and relative rank of hydrogen cyanide and cyanide compounds in the 1991 TRI. Table 4.7 lists the top four industries that emitted the largest quantities of 33/50 cyanide compounds and their total reported releases and transfers.

In 1991, the chemicals and allied products industry contributed more than any other industry to releases and transfers of both hydrogen cyanide and cyanide compounds, accounting for almost 78 percent of the total. Further, releases and transfers reported by facilities that produce hydrogen cyanide accounted for nearly 21 percent of the total emissions of hydrogen cyanide reported by the chemicals and allied

products industry. The primary metals industry also contributed a significant fraction (more than nine percent) of the total releases and transfers of cyanide compounds.

USES OF THE 33/50 CYANIDE COMPOUNDS

Hydrogen cyanide is used as a reagent to manufacture methyl methacrylate, acrylonitrile, adiponitrile, and sodium cyanide. A large number of other uses, all relatively small in consumption of hydrogen cyanide, include the manufacture of ferrocyanides, acrylates, ethyl lactate, lactic acid, chelating agents, laundry bleaches, and pharmaceuticals.

Sodium cyanide is used to extract gold and silver from low grade ores in mining operations. It is also used extensively in the electrodeposition of gold, silver, copper, zinc, brass, and cadmium. Also, sodium cyanide is used in the manufacture of intermediates for later chemical synthesis of pharmaceuticals, dyes, vitamins, and plastics.

The uses of hydrogen cyanide and sodium cyanide are illustrated in a chemical-use tree diagram shown in Figure 4.1.[14] The numbers along each branch of the chemical-use tree are weight fractions of the usage of the chemical or product in the first box to produce the chemical or product in the second box. For example, in Figure 4.1, ten percent of the hydrogen cyanide produced is used to manufacture sodium cyanide; 90 percent of the sodium cyanide produced is used to extract precious metals from their ores.

Some of the use clusters that incorporate the 33/50 cyanide compounds into their formulations, or rely upon them in the manufacturing process, also use other 33/50 chemicals in their manufacture. Methyl methacrylate products fall into the use clusters of plastics and resins, which includes materials that are manufactured from the 33/50 aromatics. Plastics and resins were selected for substitutes evaluation as discussed in Chapter 2.

ENDNOTES

[1] Hampshire Research Assoc., Inc., *Toxics in the Community*, US EPA, Office of Toxic Substances, Economic and Technology Division, (Washington: GPO, September, 1991).

[2] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed. (New York: John Wiley, 1993), Vol. 7.

[3] "Sodium Cyanide," *Hazardous Substances Data Bank*, November 9, 1990.

[4] Ibid.

[5] "Hydrogen Cyanide," *Hazardous Substances Data Bank*, April 27, 1992.

[6] Ibid.

[7] Ibid.

[8] "Chemical Profile: Hydrogen Cyanide," *Chemical Marketing Reporter*, June 18, 1990.

[9] "MMA Chemical Profile," *Chemical Marketing Reporter*, January 14, 1991.

[10] "Sodium Cyanide Market Turns Around in a Hurry," *Chemical Marketing Reporter*, February 11, 1991.

[11] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., (New York: John Wiley, 1993), Vol. 7.

[12] *Chemical Marketing Reporter*, August 2, 1993.

[13] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., (New York: John Wiley, 1993), Vol. 7.

[14] Sources for Figure 4.1:
"Hydrogen Cyanide," *Chemical Marketing Reporter*, May 24, 1993.
"MMA Chemical Profile," *Chemical Marketing Reporter*, January 14, 1991.
"NaCN Oversupply Leads HCN to Other Outlets," *Chemical Marketing Reporter*, August 2, 1993.
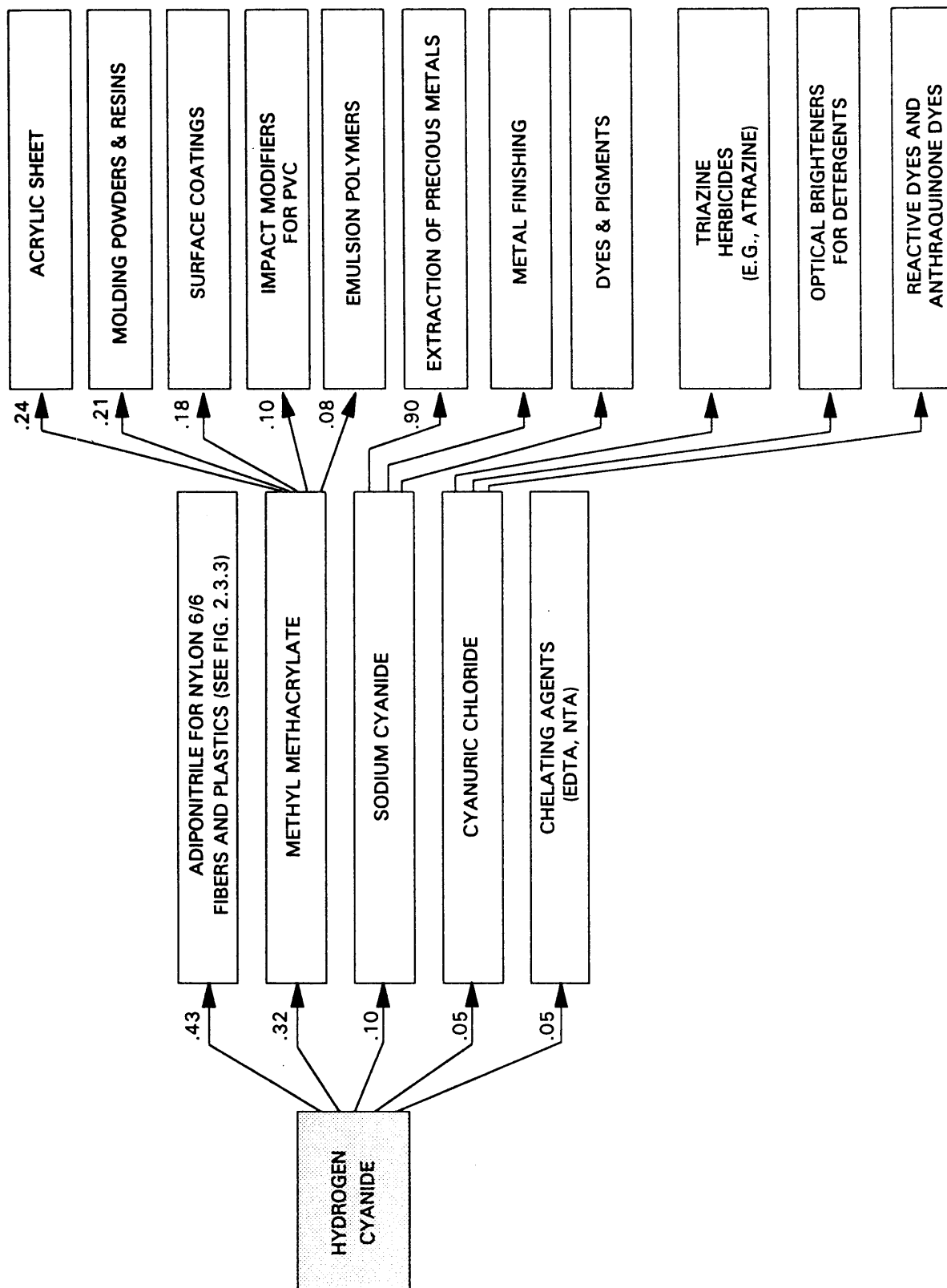
FIGURE 4.1   CYANIDES

NOTE: Reliable data were not available to estimate weight fractions along some branches of the chemical-use tree.

formulation has specific characteristics and various 33/50 metal applications. A brief description of these is presented below.

Primary alkaline and zinc-carbon (also called Leclanche) cells both use zinc as the anode, manganese dioxide (MnO_2) as the cathode, and an electrolyte separating the two electrodes. The alkaline cells utilize a powdered zinc anode and a potassium hydroxide (KOH) solution as the electrolyte; the zinc-carbon anode is solid zinc and the electrolyte is an ammonium chloride-zinc chloride matrix. The zinc-carbon cell was the first so-called dry cell battery due to the application of gelatin, agar, and flour in the electrolyte matrix to make it spill proof. Until recently, mercury was added to alkaline and zinc-carbon batteries to inhibit hydrogen gas evolution on the zinc electrode, thus preventing the effects of hydrogen - increased internal electrical resistance and corrosive reactions.[1] A build-up of gas can also break the safety vents provided on batteries to prevent explosion from excessive gas pressure. Once the safety vents are broken, the corrosive electrolyte can leak out and the cell will no longer function. Reduction and elimination of this use of mercury by industry has been significant.

The zinc-silver cell, commonly known as the silver cell, is another battery system which utilizes zinc as the anode. A silver oxide (Ag_2O) material is used as the counter electrode. This system, most commonly a button cell design, replaces zinc-mercuric oxide button cells in specific constant-voltage uses due to its improved operating conditions. Mercury is still added to the anode of this battery to prevent hydrogen gas evolution. Current applications of silver cells include watches and calculators.[2]

Zinc-air batteries utilize air as the cathode oxygen source rather than a metal oxide electrode (e.g., MnO_2). The anode is zinc powder typically mixed with an electrolyte solution of KOH. This design for the zinc-air battery presents advantages and disadvantages over other battery systems. Because the oxygen in the air functions as the cathode, the space within the cell normally occupied by the metal oxide can now be filled with more zinc, thus increasing the battery's useful life. To allow the flow of air into the cell, ventilation holes are added to the battery's casing. These holes, while allowing the free passage of air into the cell, also allow any hydrogen gas generated at the zinc anode to escape. Therefore, the need for mercury at the anode is reduced, and has been eliminated at least by one battery manufacturer (Eveready). The main disadvantage is that once the ventilation holes are unsealed for use, the cells continually discharge because the flow of air is continuous. Therefore, zinc-air batteries are utilized in continuous use applications.[3]

Primary cells which use mercury compounds as an electrode are commercially known as "heavy duty" batteries. The electrode materials are mercuric oxide with graphite (cathode) and powdered zinc (anode).[4] These cells typically contain 40 percent by weight mercury, present both as an electrode and gas inhibitor. Their applications are usually associated with hospital facilities where a constant voltage discharge is required over the entire life cycle of the battery. Advances in alkaline and other primary batteries, however, have significantly impacted the need and availability of the heavy duty cells. Manufacturing of these batteries occurs outside the U.S., and only a limited number of companies choose to distribute them here.

Another primary cell configuration is the lithium battery, which has a lithium anode. Lithium batteries use a variety of cathode and electrolyte materials, and are classified according to the state of the cathode, either liquid or solid. Liquid cathodes of sulfur dioxide (Li-SO_2) and thionyl chloride (Li-$SOCl_2$) also serve as part of the liquid electrolyte of the cell. Solid cathode cells include carbon monofluoride (Li-CF), manganese dioxide (Li-MnO_2), iron disulfide (or iron pyrite, Li-FeS_2), and iodine (Li-I_2) and contain liquid electrolyte. The liquid electrolyte of both liquid and solid cathode cells is one or a combination of many lithium metal salts in an organic solvent. The applications for lithium batteries vary, and include heart pacers and other low drain applications. Button cells of Li-FeS_2

CHAPTER 5

BATTERIES

Batteries are an integral part of modern, everyday life - from their use in portable appliances to lead-acid automotive batteries. All of the 33/50 metals except chromium (i.e., cadmium, lead, mercury, nickel) are used in battery fabrication, with batteries representing the single largest use of lead and cadmium. The use of mercury has declined substantially in recent years, however, due to product redesign initiated by the battery manufacturing industry. This chapter presents the uses of 33/50 metals and metal compounds in batteries, substitutes for the 33/50 metals, and the accomplishments of the battery industry to reduce mercury use in batteries.

Batteries represent the single largest uses of lead and cadmium, and, until recently, were among the largest uses of mercury. Today, health and environmental concerns, combined with legislative mandates, have spurred battery manufacturers to redesign their products to greatly reduce the use of mercury.

INDUSTRY PROFILE

A battery is a device that converts chemical energy into electrical energy. Primary batteries allow only one continuous or intermittent discharge of electrical energy because the chemical reaction that supplies their current cannot be reversed. Secondary batteries can be recharged by passing a direct current through the cell in the opposite direction to the current flow on discharge. Recharging the cell regenerates the active chemicals within the cell by reversing the chemical reaction that occurs during discharge. Secondary batteries are also called storage batteries. Primary batteries are available in configurations of "AAA," "AA," "C," "D," 9-volt, and button cells. Secondary battery configurations include 12 volt lead-acid batteries and AAA, AA, C, D, and 9-volt NiCd batteries. Primary and secondary batteries are discussed further in the sections below.

Primary Batteries

Primary batteries include alkaline, zinc-carbon, zinc-air, silver, mercuric oxide (heavy duty), and lithium cells. Each battery

TABLE 5.2   YEARLY MERCURY CONSUMPTION IN BATTERIES

Year	Consumption (short tons)	Percent of Total	Percent Change
1983	887.4	47.5	-
1984	1128.6	54.3	+27.2
1985	1049.6	55.4	-07.0
1986	827.0	47.3	-21.2
1987	587.6	36.9	-29.0
1988	493.5	29.8	-16.0
1989	275.6	20.6	-44.2
1990	116.9	14.7	-57.6
1991	19.8	3.2	-83.0
1992	17.6	2.6	-11.1

Source:
U.S. Bureau of Mines, Dept. of the Interior, 1993

Price of Batteries

Primary batteries have much lower initial cost than secondary batteries. In addition, secondary batteries have the added cost of a battery charger. Secondary batteries are the more economical option, however, when the cost is spread over the expected life of the battery. Table 5.3 presents the price of primary alkaline and secondary NiCd household batteries and the price of lead-acid automotive batteries.

> *Cadmium, lead, nickel, and mercury are all used as electrodes in battery designs. Mercury is also used as an additive in cells with zinc electrodes, although this use of mercury has decreased substantially in recent years.*

TABLE 5.3   PRICES OF BATTERIES

Battery Size	Price Range[a] ($/battery)		
	Alkaline	NiCd[b]	Lead-Acid
9V	0.50 to 2.36	5.00 to 6.96	N/A
D	0.50 to 2.36	3.35 to 3.48	N/A
C	0.50 to 2.36	3.35 to 3.48	N/A
AA	0.50 to 2.54	2.24 to 2.75	N/A
AAA	0.62 to 2.39	2.35 to 2.74	N/A
12V (automotive)	N/A	N/A	29.97 to 89.95

[a] Price ranges are approximate, based on prices in Knoxville, Tennessee area
[b] Prices for NiCd battery rechargers range from about $8.47 to $29.95
N/A: Not Available

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and Li-I$_2$ have replaced significantly the uses of silver cells and alkaline batteries, respectively, in low drain, long life applications.[5]

Secondary Batteries

The largest segment of the U.S. battery market is the lead-acid storage battery used for automotive starting, lighting, and ignition (SLI). SLI batteries supply current for operation of the cranking motor and the ignition system when the engine is being cranked for starting, and for lights and electrical accessories when the generator is not operating fast enough to handle the electrical load. Besides their use as automotive batteries, lead-acid batteries are used as industrial standby and traction batteries. Sealed lead-acid batteries are used in security and alarm systems, for emergency lighting, and in consumer products as a cordless, portable power supply.

Secondary alkaline cells contribute 20 percent of the worldwide secondary battery market, but have traditionally been used in only highly specialized, military applications.[6] However, advances in the technologies of rechargeable alkaline cells have resulted in the recent marketing of these cells in the consumer market. NiCd batteries are the best known secondary alkaline battery. NiCd cells use a cathode of nickel oxide and an anode of cadmium. Sealed NiCd batteries find extensive use in portable appliances, calculators, and computers where

high rate power drains are experienced. Sintered plate NiCd batteries are used in extremely high discharge rate functions like starting small jet and helicopter engines or auxiliary power units in large military jets and helicopters. Sintered NiCd batteries are also used to provide emergency power for critical electrical systems. New designs have extended their applications in electric vehicles where NiCd cells represent 20 percent of the secondary battery market.

Quantity of 33/50 Metals Used in Batteries

Table 5.1 presents the total weight of lead, mercury, cadmium, and nickel consumed in all applications in 1992 and the weight and percentage of these metals consumed in battery fabrication (calculated from chemical-use trees). Battery consumption of cadmium has increased from 36 percent in 1989 to 55 percent in 1992. U.S. Bureau of Mines data indicate that the amount of mercury used in household batteries decreased 92 percent between 1984 and 1989. Table 5.2 traces this dramatic change in mercury consumption in batteries from 1983 to 1992. Conversely, the amount of lead used in the typical lead-acid automotive battery has increased in recent years to 22 pounds. Manufacturers have increased the lead content in response to demand for better cold-cranking power and longer battery life.

TABLE 5.1 QUANTITY OF 33/50 METALS CONSUMED IN BATTERIES

1992 Short Tons			
33/50 Metal	Total Weight Consumed	Total Weight in Batteries	% in Batteries
Lead	1,336,300	1,073,050	80.3
Mercury	685	17.8	2.6
Cadmium	4,102	2,225.6	55
Nickel	130,700	<650	<0.50

lead produced in the U.S. is used to manufacture lead batteries, a significant portion of the primary lead industry emissions can be attributed to batteries. Using the same principle, portions of the emissions from the production of nickel and cadmium can also be attributed to the battery manufacturing process.

Environmental Releases of 33/50 Metals from Battery Manufacturing

The storage battery and primary battery manufacturing industries are classified under SIC codes 3691 and 3692, respectively, and are required to report their environmental releases and transfers in TRI. Table 5.4 presents the 1991 TRI data for SIC 3691. Table 5.5 lists the 1991 TRI data for SIC 3692. Releases and transfers of 33/50 metals reported by these industries in 1991 were more than 2.6 million pounds. As with releases from the primary non-ferrous metals industry, lead and lead compounds were the primary pollutants, contributing almost 37 percent of the total. Off-site transfers were by far the largest categories of environmental releases of the 33/50 metals from battery manufacturers, followed by on-site releases to air.

Environmental Releases of the 33/50 Metals from Battery Recycling

Lead-acid batteries are the only batteries that are currently recycled on a large scale. Recycled lead supplied 65 percent of the lead produced in the U.S. in 1988.[9] This share of lead production from recycled feed has been increasing since 1983.[10] Government studies show lead-acid battery recycling rates peaking at 87.3 percent in 1980, declining to a low of 58.5 percent in 1985 and rebounding to 80 percent by 1987. Estimates placed the lead-acid battery recycling rate at more than 90 percent for 1989 and 1990. With nearly 1.1 million short tons of lead used in battery fabrication, a recycling rate of 95 percent indicates more than 110 million pounds of lead is unaccounted for each year, perhaps being disposed of in landfills or being stored by the consumer.

Reclaimed lead batteries are typically sent to factories where the lead, sulfuric acid, and plastics (polypropylene case and PVC separators) are separated. The acid is reused as a component of fertilizer or neutralized for disposal. The polypropylene is chipped and sold to reprocessors and the PVC is usually discarded. The lead is smelted into ingots. Slag from the smelting process contains three to five percent lead that must be disposed of, usually as hazardous waste.[11]

The secondary lead smelting industry is classified under SIC 3341. Table 5.6 presents the 1991 TRI data for lead and lead compound releases from SIC 3341. Nearly 96 percent of the lead released from lead smelters was sent to land-based disposal facilities off-site.

> *Environmental releases of the 33/50 metals occur from metal mining and refining, battery manufacturing and recycling, and the disposal of spent batteries as municipal solid waste. Rechargeable NiCd batteries have accounted for more than half of the cadmium discards in municipal solid waste since 1986.*

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

The 33/50 metals and metal compounds are toxic chemicals that cause both acute and chronic health effects. Long-term exposure to the 33/50 metals may cause organ damage, or, in some cases, cancer. Chapter 1 discussed the health effects from exposure to metals in more detail. Potential environmental effects due to the disposal of batteries are summarized below.

Municipal solid waste is disposed of by incineration or in landfills. Problems from the disposal of batteries are present when the discarded batteries are burned. The air pollution caused by incineration has the potential to emit mercury vapor, and the incinerator ash that is usually disposed of in a landfill often contains

DESIRED PROPERTIES OF BATTERIES

The efficacy of batteries is evaluated using a number of parameters. Some of the more important ones are the cycle life, energy density, nominal voltage, self-discharge rate, and specific energy of the battery. Cycle life is the number of discharge-charge cycles that a rechargeable battery will achieve before failure. Energy density is used to express the stored energy as a function of battery volume. Nominal voltage is the expected voltage of a fully-charged battery at a specified discharge rate and temperature. Self-discharge rate is the percentage capacity loss per unit time for a battery during periods of nonuse. Specific energy is the stored energy as a function of the weight of the battery.[7]

Consumers prefer an economical household battery that can be used in many applications, has a good shelf life, and is economical. Traditionally, primary batteries have met these needs, but rechargeable household batteries are gaining a larger market share as rechargeable battery technologies improve. In 1988, the rechargeable battery market was growing at 15 percent per year, more than double the annual growth rate that primary batteries were experiencing. In 1993 the overall rechargeable market was still at a 10 to 15 percent annual growth rate. Some sources predict an annual growth rate of near 30 percent by 1997 when improved battery technologies become commercialized.[8]

The growth in the rechargeable market is attributed to the improved capacity of a typical rechargeable cell and decreased internal resistance of the cell that allows more power to be delivered faster. Rechargeable batteries have also benefitted from an increase in the efficiency of electric motors that adds to battery efficiency. Improvements and diversity of available battery rechargers, as well as consumer concerns about the disposal of spent primary batteries, have contributed to a gain in market share for rechargeable batteries.

Automotive batteries must meet additional criteria, because of the short heavy loads they must supply, and the temperature extremes to which they are subjected. Therefore, automotive batteries are designed to provide a high electrical output and to have the ability to withstand sub-zero or elevated temperatures.

ENVIRONMENTAL RELEASES OF 33/50 METALS FROM PRODUCTION, USE, AND RECYCLING OF BATTERIES

Environmental releases of the 33/50 metals and metal compounds from battery fabrication occur from metal mining and refining through recycling or disposal of spent batteries. The following sections present the environmental releases from the production of 33/50 metals, the battery manufacturing process, and the recycling of spent batteries.

Environmental Releases from Production of the 33/50 Metals and Metal Compounds

Releases and transfers of the 33/50 metals and metal compounds from the primary non-ferrous metals industry were discussed in Chapter 1. Total reported environmental releases of cadmium, lead, nickel, mercury, and their compounds in 1991 were almost nine million pounds. Lead and lead compounds contributed more than 8.2 million pounds (92 percent) of these releases. Nickel and nickel compounds accounted for the next largest fraction (six percent) of the releases and transfers from the primary nonferrous metals industry, but only a small fraction of the nickel produced in the U.S. (less than one percent) is used to manufacture batteries. Cadmium and cadmium compound releases totalled almost 145 thousand pounds, but it is more difficult to apportion cadmium releases by end-use since cadmium is produced as a by-product of zinc refining. No releases of mercury were reported by the primary non-ferrous industry.

Using the principles of life cycle assessment and the life cycle concept, some fraction of these releases of metals and metal compounds from the primary nonferrous metals industry can be attributed to their end-use in batteries. For example, since approximately 80 percent of the

TABLE 5.5   RELEASES AND TRANSFERS OF 33/50 METALS AND METAL COMPOUNDS FROM THE PRIMARY BATTERIES MANUFACTURING INDUSTRY (SIC 3692)

Chemical	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Cadmium	2	5	0	0	7	0	250	250
Cadmium Compounds	4,082	1,715	12,181	0	17,978	261	167,266	167,527
Lead	19,472	219	305	0	19,996	1,335	61,179	62,514
Lead Compounds	89,539	5,494	8,139	245	103,417	8,025	292,528	300,553
Mercury	0	1	0	0	1	0	3	3
Mercury Compounds	236	0	26	0	262	0	660	660
Nickel	2,816	1,892	0	8	4,716	6	317,388	317,394
Nickel Compounds	8,103	4,091	22,538	47	34,779	1,191	303,163	304,354
TOTAL	124,250	13,417	43,189	300	181,156	10,818	1,142,437	1,153,255

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TABLE 5.4 RELEASES AND TRANSFERS OF 33/50 METALS AND METAL COMPOUNDS FROM THE STORAGE BATTERIES MANUFACTURING INDUSTRY (SIC 3691)

Chemical	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Cadmium	2	5	0	0	7	0	250	250
Cadmium Compounds	4,082	1,715	12,181	0	17,978	261	167,266	167,527
Lead	19,472	219	305	0	19,996	1,335	61,179	62,514
Lead Compounds	89,283	5,489	8,139	245	103,156	8,025	292,480	300,505
Mercury	0	1	0	0	1	0	3	3
Mercury Compounds	219	0	0	0	219	0	1	1
Nickel	2,816	1,892	8	0	4,716	6	317,388	317,394
Nickel Compounds	8,103	4,091	22,538	47	34,779	1,191	303,163	304,354
TOTAL	123,977	13,412	43,171	292	180,852	10,818	1,141,730	1,152,548

Sources:
TRI, 1991
Correspondence from Hampshire Research Association, Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

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elevated concentrations of metals. For example, Warren County, New Jersey started a battery-collection pilot program in 1989 after receiving an EPA warning for high cadmium in its municipal waste incinerator ash and mercury in the stack. This rural county of only about 94,000 people collects about 1,300 pounds of batteries each month. That translates into almost 16 thousand pounds of batteries being discarded each year by one small, rural community. Extrapolating the battery-discard rate across the entire U.S. population gives an idea of the enormity of the battery disposal problem. Warren County sorts the batteries according to those to be recycled and those to be landfilled. Concentrations of leachable cadmium in the ash have not exceeded EPA toxicity testing since the battery-recycling program was initiated.[12]

Problems also exist when batteries are improperly disposed of in a landfill. Disposal of lead-acid batteries in a landfill is prohibited because the sulfuric acid can leach and contaminate groundwater. Corrosion products encased in the battery are also susceptible to leaching. Even with a recycle rate of 95 percent, lead-acid batteries have the potential to be disposed of as municipal solid waste, although some consumers may store these batteries in their garage.[13]

Rechargeable NiCd batteries have accounted for more than half of the cadmium discards in municipal solid waste since 1980. Cadmium discards in household batteries were 930 short tons in 1986 and are expected to increase unless NiCd batteries are replaced in some applications by a safer substitute, or efficient programs encouraging their collection are further implemented (as in the example above).[14]

EVALUATION OF SUBSTITUTES

The health, safety, and environmental issues associated with the use of the toxic 33/50 metals in batteries has spurred the development of a number of safer substitutes. Mercury has been almost eliminated from carbon-zinc and alkaline MnO_2 batteries, at a much faster rate than

manufacturers believed was possible just a few years ago, and at a rate that exceeds legislative mandates. Research and development on alternatives to NiCd batteries has exploded in recent years, particularly in the area of nickel-metal hydride (NiMH) and lithium rechargeable batteries. NiMH batteries are currently being used in some applications, but until recently this technology was believed to be much farther from volume production.

> By substituting new materials for mercury at the zinc anode, carbon-zinc and alkaline MnO_2 battery manufacturers have reduced or eliminated mercury from their products. In addition, alternatives to NiCd batteries are now available to the consumer as battery manufacturers strive to produce safer products.

Progress is not as rapid in identifying substitutes for lead-acid batteries that constitute the vast majority of the battery wastestream. Safer substitutes for lead-acid batteries are being developed, however, and these technologies could see rapid advancement as societal pressures to reduce the use of toxic chemicals increase.

The following sections discuss the elimination or reduction of mercury in carbon-zinc and alkaline MnO_2 batteries; substitutes for NiCd rechargeable batteries; and the status of research and development on substitutes for the lead-acid battery.

Safe Substitutes for Mercury in Carbon-Zinc and Alkaline MnO_2 Batteries

In response to legislation in several states, carbon-zinc and alkaline MnO_2 battery manufacturers have reduced or eliminated mercury from their products through material use modifications. These reductions in mercury use exceeded even legislative demands, and the industry is now initiating efforts to eliminate mercury entirely. Table 5.7 presents state legislation dates for low mercury and no mercury formulations for alkaline and zinc-carbon

TABLE 5.6   RELEASES AND TRANSFERS OF LEAD AND LEAD COMPOUNDS FROM THE SECONDARY LEAD SMELTING INDUSTRY (SIC 3341)

Chemical	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Lead	51,262	856	19,534	0	71,652	849	1,826,680	3,916,764
Lead Compounds	101,322	544	53,298	0	155,164	1,273	2,055,256	1,347,932
TOTAL	152,584	1,400	72,832	0	226,816	2,122	3,881,936	5,264,696

Source:
TRI, 1991

Zinc-carbon cells, prior to mercury reduction initiatives, contained mercury in a concentration of 100 to 150 ppm (0.01 to 0.015 percent by weight). The earliest state legislative requirement for implementation of "no mercury added" was January, 1992 (New Jersey). All manufacturers met this requirement for all zinc-carbon battery sizes by April, 1992. Surface active organic compounds which coat the zinc electrode, and potassium chromate or dichromate which forms an oxide film on the zinc, are some material substitutes to the mercury additives.[15]

Mercury free separators for both zinc-carbon and alkaline MnO_2 batteries are among the technologies allowing mercury-free battery alternatives. These technologies are proprietary to battery companies and their compositions can be found mainly in patent literature. For example: the separator for zinc-carbon batteries has kraft paper coated by a polymer or polymer fiber layer. The layer can be polyamide, polyvinyl alcohol, polyvinyl acetate, polyethyleneimine, urea-formaldehyde polymers, or amine-formaldehyde polymers.[16] The separator for the alkaline MnO_2 battery made of woven or nonwoven polymeric fibers is coated on one or both sides with a gel, (e.g., carboxymethylcellulose, CMC), modified starch, polyvinyl alcohol, or hydroxypropyl cellulose. The zinc anode has no mercury or cadmium and contains 0.005 to 1 percent iodine and 1 to 1000 ppm of stabilizer, e.g., an ethoxylated fluoroalcohol or mercaptan and polyethoxylated alcohol.[17] Another example is alkaline MnO_2 batteries containing HO-terminated perfluoroalkylpolyoxyethylenes corrosion inhibitors. The inhibitors are $CF_3(CF_2)_mSO_2NR(CH_2CHR'O)_nH$, where m=1-20, n=3-30, $R=C_{1-10}$ alkyl, and R' = H or Me, and have molecular weight of 500 to 2500. The zinc alloy contains iodine, <0.1 percent mercury, and optionally lead, aluminum, bismuth and/or calcium.[18]

Safe Substitutes for Mercury in Button Cell Batteries

Most button cell designs that include mercury as an additive to suppress hydrogen gas evolution, including alkaline, zinc-carbon, silver oxide, and zinc-air, have not been included in state legislative requirements. Typical mercury contents of these batteries range from 1 to 24 milligrams per cell. Even without legislative requirements, battery manufacturers are attempting to eliminate the added mercury from these cells as well. For example, Eveready has recently marketed a zinc-air cell that has zero mercury added.

Zinc-mercuric oxide button cells which use mercury as an electrode material have been the subject of legislation, however. Since 1992, bans on the sale of zinc-mercuric oxide button cells and requirements for the collection (the responsibility of the manufacturer or point-of-sales) of these cells have existed in many states. Table 5.8 presents the state regulations for the mercuric oxide button cells.

Safe Substitutes for Mercuric Oxide Heavy Duty Batteries

In the case of mercuric oxide heavy duty batteries, mercury is present as an electrode material. The mercury content of these batteries is typically 35 to 40 percent by weight. With improvements in other battery designs (both alkaline and zinc) that meet the operating characteristics and performance requirement of the mercuric oxide battery, manufacturers expect the complete phase-out of these batteries from civilian applications. Military applications, representing a large sector of this market, may, however, continue to use these cells.

Safe Substitutes for Nickel-Cadmium Batteries

Like the mercuric oxide in heavy duty primary batteries, the cadmium or nickel in NiCd batteries cannot be reduced since they are the active components of the battery. Thus, alternative electrode materials that are environmentally non-hazardous should be considered. Nickel-metal hydride rechargeable batteries use a new battery chemistry that has a metal hydride electrode as a replacement for some applications of NiCd batteries. Rechargeable lithium batteries, another

batteries. Most legislative requirements and manufacturer accomplishments apply to batteries of all sizes.

Prior to legislation and manufacturer initiatives, typical alkaline batteries contained 0.8 to 1.2 percent mercury (by weight) as an additive to suppress gassing at the zinc electrode. Mercury was used to combine with the zinc anodic material and form a zinc/mercury amalgon. This reduced the rate at which the zinc oxidized with the alkaline electrolyte, thus

reducing the generation of hydrogen gas. By substituting new materials for mercury at the zinc anode, each U.S. alkaline battery manufacturer was able to meet the "250 ppm" and "no mercury added" requirements of state legislation. By May of 1991, all manufacturers met the "250 ppm" requirement, one year ahead of legislative requirements. By the end of 1993, all alkaline battery manufacturers had met the "no mercury added" requirements, three years ahead of any state legislative requirements.

TABLE 5.7   STATE LEGISLATIVE DATES FOR LOW MERCURY/NO MERCURY FORMULATIONS FOR ALKALINE AND ZINC-CARBON BATTERIES

State	Alkaline		Zinc-Carbon
	250 ppm (0.025%) Mercury	No-Mercury Formula	No-Mercury Formula
Federal (proposed)	---	1-1-96 (mfg. date)	1-1-95 (mfg. date)
Arkansas	---	1-1-96 (mfg. date)	1-1-94 (mfg. date)
California	1-1-94 (mfg. date)	1-1-96 (mfg. date)	1-1-94 (mfg. date)
Connecticut	1-1-92 (mfg. date)	---	1-1-93 (mfg. date)
Florida	7-1-93 (sale date)	1-1-96 (sale date)	1-1-96 (sale date)
Iowa	7-1-93 (sale date)	1-1-96 (sale date)	---
Maine	1-1-94 (sale date)	1-1-96 (sale date)	1-1-93 (sale date)
Minnesota	2-1-92 (mfg. date)	1-1-96 (sale date)	---
New Hampshire	1-1-93 (mfg. date)	1-1-96 (sale date)	1-1-93 (mfg. date)
New Jersey	1-1-92 (mfg. date)	1-1-96 (mfg. date)	1-1-92 (mfg. date)
New York	1-1-92 (mfg. date)	---	1-1-93 (mfg. date)
Oregon	1-1-92 (mfg. date)	---	---
Rhode Island	1-1-92 (mfg. date)	---	---
Vermont	2-1-92 (mfg. date)	1-1-96 (sale date)	---
Wisconsin	---	1-1-96 (mfg. date)	7-1-94 (mfg. date)

Source:
National Electrical Manufacturers Association, 1993

cobalt, aluminum, and manganese (Mm, Ni, Co, Al, Mn), the electrode achieves a service life about 100 times greater than that of LaNi$_5$. Sanyo is developing an optimum component ratio for these types of alloys. The AB$_2$ type of alloys are also known as the Ovonic metal hydrides alloys. These alloys are based on vanadium, nickel, zinc, and titanium, and they are proprietary to and patented by The Ovonic Battery Company (USA). Some of the advantages of the Ovonic batteries include higher energy density, the absence of memory effect, and the reduction of environmentally and ecologically toxic and hazardous elements. Ovonic batteries compare favorably with NiCd batteries on a dollar per Amperehour basis. Ovonic battery technology has been licensed to a number of companies such as Varta AG (Germany), the largest European battery manufacturer, Hitachi Maxell (Japan), and Goldpeak Industries (Hong Kong).

Recently, Varta AG, Toshiba Battery Company (Japan), and Duracell International Incorporated (USA) have signed an agreement to develop, standardize, and market NiMH batteries. Goldpeak has been marketing some types of NiMH batteries since 1990. Gates Energy Products began marketing a "C" size 2300 mAh nickel-metal hydride cell in 1991. The Portable Battery Division of Gates Energy Products, Gainesville, Florida, is responsible for marketing the nickel-metal hydride batteries. Sanyo is marketing an electric shaver powered by nickel-metal hydride batteries. The Sanyo-developed nickel-metal hydride battery has an energy density approximately 1.8 times that of the conventional NiCd cell, while it can be charged/discharged up to 500 times.

Lithium Batteries. Rechargeable lithium batteries are also being developed as possible substitutes for NiCd batteries. The rechargeable lithium cells have the advantages of high energy density, high cell voltage, and good capacity retention. The weak points of the rechargeable lithium cells are a limited cycle life (typically 100 to 200 cycles), difficulty in applying a fast charge to the cells, and safety concerns due to the lithium metal flammability. During cycling,

lithium deposition on charge is more or less dendritic, mossy, and porous. This causes losses of lithium by reaction with the electrolyte, or separation of particles from the electrode substrate, resulting in short circuiting through the separator. The solutions to these problems, besides a suitable stable electrolyte, are the use of the following: 1) a large excess of lithium; 2) a large surface area to decrease the current density; and 3) a microporous separator to prevent dendrites. This separator is one of the key-points for lithium cell development.

Positive new developments in lithium rechargeable cell technology include a lithium-ion technology and a lithium polymer cell. The lithium-ion system eliminates the use of metallic lithium as the anode, and uses carbon and metal oxides, the electrolyte and cathode materials, to initiate the chemical reaction. Lithium is present within the carbon's molecular structure which represents the micro-porous separator. Sony Energytec announced its lithium-ion cells generate four times as much energy as nickel-cadmium batteries. Lithium polymer systems use a polymeric electrolyte in a solid state cell to eliminate the weak points of the traditional rechargeable lithium cells. The presence of the polymer, representing the microporous separator, prevents the recharging reaction from speeding out of control. Prototypes of these batteries are claimed to last four times as long as nickel-cadmium batteries.[19]

Reusable Alkaline Batteries. In September, 1993, Rayovac began marketing the first reusable alkaline battery called Renewal. This new battery design functions like traditional alkaline batteries, but can be recharged at least 25 times. The design and chemical formulation, which is patent-protected, varies from traditional, non-rechargeable alkaline batteries, and is cadmium free and 99.975 percent mercury free ($<$ 250 ppm mercury). The life-time of each charge of the Renewal battery is as long as traditional alkaline batteries, and up to three times longer than current NiCd technologies. And, unlike NiCd rechargeable batteries, reusable alkaline batteries can retain a charge for up to five years. The recharging units,

TABLE 5.8   STATE REGULATIONS FOR MERCURIC OXIDE BUTTON CELLS

Jurisdiction	Status of Legislation	Effective Date		Note(s)
		Ban	Collection	
Federal	Not yet introduced	1-1-95	---	---
Arkansas	Passed	1-1-94	---	---
California	Passed	1-1-94	---	---
Connecticut	Passed	---	1-1-92	b,c
Florida	Passed	10-1-93	---	---
Iowa	Passed	---	7-1-96	a,b
Maine	Passed	1-1-93	---	---
Maryland	Passed	---	7-1-94	a
Michigan	passed	---	1-1-98	d
Minnesota	Passed	2-1-92	---	---
New Jersey	Passed			a
Hearing Aid Dispensers		1-1-94	Until 1-1-94	---
All others		1-20-92	---	
Rhode Island	Passed	1-1-93	---	---
Vermont	Passed	1-1-93	---	---

Source:
National Electrical Manufacturers Association, 1993
[a] Battery manufacturers financially responsible for collection, transportation, disposal, consumer education, etc.
Failure to meet these requirements results in a sales ban for the manufacturers's mercury button cells.
[b] Battery manufacturers not expressly responsible, but retailer required to collect.
[c] Battery manufacturers not expressly responsible, but state regulatory agency to issue regulations.
[d] $2/battery required at time of sale, unless trade-ins of used batteries made at that time.

alternative to NiCd batteries, offer a complete change in electrode materials. Both battery alternatives, discussed further below, are now commercially available.

Nickel-Metal Hydride Batteries. Two general classes of metallic alloys have been utilized as the basis for the nickel-metal hydride negative electrode. These are rare earth/nickel alloys generally based around lanthanum nickel alloys ($LaNi_5$ - the so called AB_5 class of alloys) and alloys consisting primarily of titanium and zirconium (designated as AB_2 alloys). By substituting cobalt for some nickel in $LaNi_5$ and misch metal (Mm), which is a mixture of some rare earth elements, it is possible to increase the life span of the batteries significantly. By eliminating the nickel portion in favor of a multicomponent alloy of misch metal, nickel,

TABLE 5.9   COMPARISON OF RECHARGEABLE BATTERY CHEMISTRIES

	Sealed Lead	High-Performance Nickel-Cadmium	Current Nickel-Metal Hydride	Rechargeable Lithium	Reusable Alkalines
Typical Product Size (mAh)	D:2500	AA:800	AA:1100	AA:500	AA:2300
Nominal Voltage	2.0	1.2	1.2	3.0	1.5
Energy Density (Wh/l)	90	130	175	300	300
Specific Energy (Wh/lb)	27	45	60	80	N/A
Cost	Low	Medium	High	High	Medium
Recharge Cycles	200	500	500	>200	25
Peak Power	Moderate	High	Moderate	Low-Moderate	Low-Moderate
Development Status	Proven	Proven	Proven	R&D	Proven
Availability	Good	Good	Limited	Very Limited	Good
Elements of Concern	Pb	Ni, Cd	Ni, La, Ce, V Co, Cr, Nd	As as LiAsF$_6$ various organics Co, Cr, V	Hg

Source:
Reinhardt Kraussm, "High Energy Batteries," *Popular Science*, February 1993
N/A: Not Available

"Renewal Power Stations," can recharge four AA or AAA batteries (portable station - $15.00) or any configuration of eight batteries (table top station model - $30.00). The time required to recharge these batteries ranges from three to five hours (sizes AA and AAA) to overnight (sizes C and D). Rayovac recharging units for the Renewal are specifically designed for these batteries, including a computer chip which senses when a battery is fully charged. SLM, a battery marketer, has recently marketed a recharger that can recharge either alkaline or NiCd batteries. Renewal battery prices range between $5.00 and $6.00 for C and D two-packs or AA and AAA four-packs.[20]

Comparison of Secondary Batteries. Table 5.9 is a comparison of sealed lead, NiCd, current NiMH, rechargeable lithium battery, and reusable alkaline battery chemistries for typical battery sizes. Rechargeable lithium or NiMH batteries are expected to meet or exceed the performance of sealed lead and NiCd batteries in the areas of energy density, specific density, and nominal voltage. Increased energy density means longer run times between charges which can make these batteries preferable in certain applications. Low rate power drain applications, such as computers, camrecorders, cellular phones, and pagers can utilize these new battery systems. NiMH batteries, however, cannot deliver the necessary current to operate high rate power drain products like power tools. Another problem with these batteries lies in their high costs. The battery industry reports that NiMH batteries cost about twice as much as NiCd batteries, which would have significant impact on the marketability of lower-cost rechargeable products.[21] Furthermore, these battery substitutes still contain elements of concern, although the 33/50 metals have been reduced/eliminated. For example, arsenic which is a potential ingredient of some rechargeable lithium battery chemistries is an acute poison. The recyclability of the rare earth metals used in the metal alloys of NiMH batteries has been questioned.

Safe Substitutes for Lead-Acid Batteries

Possible safe substitutes for lead-acid automotive batteries are primarily in the research and development stage. In the near term, NiCd batteries or nickel-zinc (NiZn) batteries could be employed to replace lead-acid batteries. Future lead-acid battery substitutes may include the nickel-iron (NiFe) battery or the sodium-sulfur (NaS) battery. As safe substitutes for products made from or containing the 33/50 chemicals in their formulation, NiCd batteries are not acceptable alternatives for lead-acid batteries and are not discussed here. Substitutes that contain nickel also do not eliminate the use of the 33/50 metals, but have been the subject of substantial research and development.

NiZn batteries could be substituted for lead-acid batteries in the near-term, but they do not have equivalent performance qualities. NiZn batteries have a lower specific energy and a limited cycle life (50 to 200 discharge-charge cycles, compared to about 750 for lead-acid). NiZn batteries also cost two to three times more than an equivalent lead-acid battery.[22]

Research and development of the NiFe battery is at the pilot plant stage. The NiFe battery has mainly been evaluated as a possible advanced battery for use in electric vehicles. In that application, the NiFe battery provides 1.5 to 2 times the vehicle range of the lead-acid battery. A primary disadvantage of the NiFe battery is that the battery system must include a system for regular watering and the removal of hydrogen gas generated during recharging.[23] In addition, cost is higher for the NiFe battery.

NaS batteries are still under development. These batteries use a ceramic beta-alumina electrolyte tube with a sodium anode and a molten sulfur cathode on opposite sides within a sealed, insulated container. NaS batteries have potential safety problems due to the reactivity of sodium and their high operating temperatures (350 to 380°C). NaS batteries are expected to be economical because they are made from expensive materials and have a long projected service life.[24]

ENDNOTES

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[2] Ibid.

[3] *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th ed., (New York: John Wiley, 1993), Vol. 3.

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Conclusions

Substantial progress has been made in the design and manufacture of batteries that do not contain 33/50 metals. Most of the successful research, however, has been limited to developing safe substitutes for the mercury and cadmium used in batteries. The development of low-mercury and mercury-free batteries should eliminate batteries as one of the largest sources of mercury in the nation's household hazardous wastestream. Nickel-metal hydride and lithium batteries have been introduced as alternatives to the batteries employing a cadmium electrode. It appears, however, that little or no efforts are underway to identify substitutes for the nickel electrode, except with rechargeable lithium batteries. The rechargeable lithium battery will not be without potential health and environmental effects, however, if these batteries contain arsenic.

Although lead-acid batteries contribute a significantly greater amount of environmental releases and transfers from their manufacture, use and disposal, research on safe substitutes for lead-acid batteries has not been as successful. Nonetheless, several substitutes for lead-acid batteries are currently being evaluated that may be viable alternatives. Industry responded rapidly when it became apparent that restrictions would be placed on the amount of mercury allowed in batteries. Concerns about the health and environmental effects of cadmium were probably also instrumental in hastening the development of the NiMH battery. Similar concerns about lead-acid batteries may hasten the development of suitable substitutes.

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parts. For example, the textile industry uses electroplating to increase the corrosion resistance of metal textile manufacturing equipment. The automotive industry plates parts like pistons, cylinders, pump rods, and gear shafts to increase their wear resistance. The heavy duty machinery and tools industry uses electroplating to salvage and repair equipment.[1] Manufacturers of household products use electroplating to improve the physical properties of the product or simply for decorative purposes.

Quantity of 33/50 Metals and Cyanides Used in Electroplating

Electroplating is the second largest end-use of nickel and nickel compounds, the third largest end-use of cadmium and cadmium compounds, and accounts for a substantial fraction of the annual U.S. consumption of chromium and chromium compounds. Although current data are not available, in 1989 about ten percent of the sodium cyanide produced was also used in metal finishing applications.

The quantities of cadmium, nickel, and chromium consumed in electroplating in 1992 were estimated using the chemical-use tree diagrams and the reported total annual consumption of these metals. Almost 574 short tons of cadmium was consumed in electroplating applications in 1992, representing a decline from approximately 2,000 short tons (51 percent of the consumption) in 1979.[2] The decline in the percent-use of cadmium for electroplating can be partly attributed to the increased demand of cadmium for nickel-cadmium batteries, but cadmium's use as a metal coating has also declined in recent years.

Nickel is the most widely used plating metal and has the largest annual consumption of the 33/50 metals in this application. In 1987, the U.S. consumed 22,650 short tons of nickel for electroplating purposes. Of this, 89.6 percent was sold as commercially pure nickel, and the remaining 10.4 percent was in the form of nickel salts. U.S. consumption of nickel for electroplating was 14,377 short tons in 1992.

Sodium bichromate or chromic acid are the chromium compounds commonly used to supply chromium metal ions to a plating bath. Roughly 7,405 short tons of chromium compounds were used in electroplating in 1992.

Price of 33/50 Metals and Cyanides Used in Electroplating

Electroplating baths consist of metal ions in acid, alkaline, or neutral solutions. The metal ions are usually supplied to the bath either in elemental form, as inorganic metal salts, or as other metal compounds. Table 6.1 lists the 1994 price of some of the common chemical compounds used in electrolytic solutions. The metal salts or metal compounds used to supply the metal electrolyte are typically the more expensive components of the electrolytic solution. Chemicals like sulfuric acid and the cyanide compounds are used to dissolve the metal or improve the properties of the plating bath.

DESIRED PROPERTIES OF 33/50 METALS AND CYANIDES IN ELECTROPLATING

There are a diversity of metals, metal compounds, and electrolytic solutions used in electroplating. The 33/50 metals are commonly used because of their excellent corrosion resistance, wear resistance, and decorative properties. Sodium cyanide and potassium cyanide, the cyanide compounds normally used in electroplating, are widely used because they impart desirable properties to the plating bath and can improve the properties of the metal plate.

> *The 33/50 metals are commonly used in electroplating because of their excellent corrosion resistance, wear resistance, and decorative properties. Cyanide compounds are used in plating baths to improve the properties of the metal plate.*

The desired properties of the 33/50 metals and cyanides used in electroplating applications are summarized below.

CHAPTER 6

ELECTROPLATING

Electroplating is a process for depositing a metal onto a substrate using an electrical current. The metal plate provides corrosion or wear resistance, and/or improves the appearance value of an item. Three of the 33/50 metals, including cadmium, chromium, nickel, and their compounds, and the 33/50 cyanide compounds are widely used in electroplating. Halogenated solvents are also frequently used as a cleaning step prior to electroplating (see Chapters 3 and 9). The use of the 33/50 metals and cyanides in electroplating and the associated cleaning processes results in the release and transfer of substantial quantities of toxic chemicals to the environment and contributes to the nation's hazardous waste burden.

INDUSTRY DESCRIPTION

The plating of metal onto a substrate has been practiced in industry for over a century and a half. The first metal to be used in plating was copper; hundreds of other metals and alloys are currently used including brass, cadmium, chromium, gold, iron, nickel, silver, and zinc. Today, electroplating is the most common method for depositing a metal coating on a substrate.

The electroplating industry consists of two sectors: 1) job shops or contract shops that electroplate a metal coating on metals or other materials (usually plastics) owned by a second party; and 2) manufacturers who electroplate their own products in captive shops under their own management. Job shops are classified under SIC 3471, the plating and polishing industry. Manufacturers that perform captive electroplating are usually classified under other SIC codes, depending on their final products.

> *Not only does the electroplating process result in the use and environmental release of large quantities of the 33/50 metals and cyanides, it can also result in the use and release of the 33/50 halogenated solvents. The solvents are frequently used to clean oils and grease from a substrate prior to electroplating.*

Electroplating applications range from the high-technology manufacture of printed circuit boards to the production of decorative metal

characteristics of a substrate. Nickel coatings are resistant to caustic alkalis, as well as to most alkaline and neutral salt solutions.

Cyanide Compounds

Cyanide plating baths have the advantage of accommodating a wide range of electrical current. They are also excellent for removing tarnish or undesirable films from objects to be plated. Coatings of cadmium, iron, gold, and zinc often use these compounds. The cyanides cause an even metal deposit to form that has lower sensitivity to impurities present in the electrolytic solution. Thus, metal plates can be produced with increased corrosion resistance. Generally, potassium cyanide is preferred for the plating of precious metals like gold and silver. Sodium cyanide is used more often for the less expensive metals because of its lower cost.[9]

ELECTROPLATING PROCESS DESCRIPTION

The electroplating process consists of a number of steps, including cleaning, electroplating, rinsing, and drying. Electroplating is usually done in a plating bath but brush plating is also done. The following describes the electroplating process and the characteristics of plating baths that use the 33/50 metals.

Plating Bath Process

A rack or barrel is typically used to hold the parts during the electroplating process. Rack plating is most commonly used, but barrels are used for smaller parts that can tumble freely without surface impingement. Barrel plating can also be more cost-effective for smaller parts because it allows for bulk handling.

After the parts are loaded onto a rack or into a barrel, cleaning is required to remove oil, grease, soil, and oxide films from the substrate and ensure good electroplate adhesion. The cleaning operation usually consists of one or more sequential treatments in a solvent degreaser (see Chapter 9), an alkaline solution, and an acid

solution. The rack or barrel is then positioned into the electroplating baths and direct current loads are distributed to the substrate. The charged substrates act as cathodes that reduce the metal ions from solution onto the substrate's surfaces. The metal ions in solution are replenished by the dissolution of metals from anodes in bar form or in small pieces contained within the bath, or with the addition of metal salts. Electroplated coating thicknesses usually range from 0.00025 to 0.0015 inch, and are usually dependent upon the time the part is left in the bath. Thicker coatings are sometimes required for specially designed parts or for repair of worn or improperly machined parts.[10] After electroplating, a final rinse tank is used to remove as much of the electrolytic solution as possible from the parts. The items are then dried. The rack or barrel is then sent to an unloading station, where the parts are inspected and removed from their loading devices.

The large number of electrolytic solutions used in the electroplating process can be modified with various additives. The thousands of different additives used are mostly proprietary, but can include the following: organic additives such as gelatin, milk, sugar, molasses, various aldehydes, coumarin, dextrin, furfural, and some sulfonic acids; and metallic additives such as selenium, cobalt, nickel, and molybdenum.[11] Brighteners and grain refiners are often added to the electrolytic solution to help control the metal crystal growth on the substrate.

Brush Plating

Brush plating is another metal deposition process used to electroplate a metal coating on a substrate, primarily in more specialized operations. For example, brush plating is used to repair and salvage molds, dies, shafts, and housings that are used in the heavy duty machinery and tools industry. A big advantage to brush plating is that it can be accomplished in the field without having to disassemble the damaged part. The brush electroplating process uses a portable stylus as the anode, the substrate as the cathode, and a direct-current power source. An absorbent material that contains the

TABLE 6.1   PRICES OF COMPOUNDS USED IN ELECTROLYTIC SOLUTIONS

Chemical	Price ($/lb)
Cadmium Chloride	68.48[a]
Cadmium Oxide	N/A
Cadmium Sulfate	38.40[a]
Chromic Acid	1.22
Nickel Carbonate	3.40
Nickel Chloride	1.60
Nickel Sulfamate	N/A
Nickel Sulfate	1.06
Potassium Cyanide	1.76 to 1.84
Sodium Bichromate	0.60
Sodium Cyanide	0.60
Sulfuric Acid	0.04

Source:
Chemical Marketing Reporter, February 7, 1994
[a] $/gal, 20 percent solution
N/A: Not Available

Cadmium

Cadmium is widely used as a coating for the protection of steel and iron parts and historically has been the highest-priced metal that is commonly electroplated.[3] Cadmium is the preferred choice for metal items that have to endure highly corrosive environments, such as marine or damp operating conditions. Besides its excellent corrosion resistance, cadmium is used in electroplating for its good solderability, ductility, retention of luster, its low coefficient of friction, and ease of deposition.[4] Cadmium produces a dull, easily tarnished coating and is rarely used as a decorative finish. Cadmium plate is resistant to alkaline compounds, but dissolves in most mineral acids.

Chromium

A chromium coating imparts a bright, highly reflective surface that has exceptional wear-resistant properties and high corrosion protection.[5] Chromium is almost exclusively plated over a nickel or copper/nickel undercoat for decorative or "bright" applications. The chromium prevents the nickel from tarnishing to a greenish or yellowish color and provides the nickel plating a higher wear resistance.[6] The nickel in turn helps give chromium the bright white color.[7] When high wear resistance of a part is required, a thick or "hard" chromium coating can be plated directly onto the metal. A chromium coat is reactive with the halogens and can be dissolved in halogen acids and sulfuric acid. Chromium coats are resistant to nitric acid and aqua regia.

Nickel

Nickel is used as a coating for decorative, engineering, and electroforming purposes. It is the closest to being considered the "all-purpose" metal for electroplating because the properties of electroplated nickel can be controlled and varied over a wide range.[8] Nickel can be electroplated onto a substrate to produce fully-bright, semi-bright, or satin-like decorative surfaces. Nickel, however, tarnishes in urban atmospheres and is usually plated over with chromium when appearance is important. Nickel is used for engineering purposes to improve the corrosion resistance, wear resistance, and magnetic

produce the corrosion resistant surfaces traditionally required for engineering purposes.[19] Nickel in solution is in the Ni(II) state.

In the Watts bath, the electrolyte is a mixture of nickel sulfate and nickel chloride. This produces a coating with a low hardness and high percent elongation. The Watts bath has an average nickel metal concentration of 80 g/l and an average current density of 50 ASF.

Nickel chloride is commercially formed by dissolving nickel metal in hydrochloric acid, followed by crystallization. Nickel sulfate is produced mostly as a by-product of electrolytic copper refining and by dissolving nickel metal in sulfuric acid.[20]

In the all-chloride bath, a nickel chloride electrolyte is used at a concentration of 300 g/l, which equates to 75 g/l of nickel metal. The average current density of the all-chloride bath is 50 ASF. This produces a hard coating with a high internal stress. As with the Watts bath, the nickel chloride is manufactured by dissolving nickel metal in hydrochloric acid, then crystallizing.[21]

The sulfamate bath uses nickel sulfamate at a concentration of 350 g/l as the electrolyte (65 g/l of nickel metal). The average current density of 37 ASF is the lowest of the three common nickel plating baths. The sulfamate bath produces a plating with a very high tensile strength and low internal tensile stress. The Ni(II) sulfamate solution is formed by dissolving nickel powder into hot sulfamic acid. Ni(II) ammonium sulfate was used in the past for electroplating baths, but its use is very limited in industry today.[22]

ENVIRONMENTAL RELEASES OF 33/50 COMPOUNDS FROM ELECTROPLATING [4]PROCESSES

Environmental releases of the 33/50 metals, metal compounds, and cyanide compounds associated with their use in the electroplating process occur from their refining or production through to the electroplating process and the final disposal of plated products. The following

sections present the environmental releases from the production of these compounds and the releases from the actual electroplating process.

Environmental Releases from Refining or Production of the 33/50 Metals, Metal Compounds, and Cyanide Compounds

Releases and transfers of the 33/50 metals and metal compounds from the primary non-ferrous metals industry reported in the 1991 TRI were discussed in Chapter 1. Total environmental releases and off-site transfers of cadmium, chromium, nickel, and their compounds were about 692 thousand pounds. Using a life cycle perspective, some fraction of these production releases can be associated with the electroplating industry. Similarly, some of the releases of cyanides from facilities that produce hydrogen cyanide, sodium cyanide, or potassium cyanide are associated with the use of these chemicals in electroplating baths. The 1991 releases and transfers of hydrogen cyanide and sodium cyanide from production facilities were discussed in Chapter 4 and totalled more than 1.4 million pounds. Most (90 percent) of these releases and transfers were from the production of hydrogen cyanide. Hydrogen cyanide is not used in electroplating baths, but about ten percent of the hydrogen cyanide produced is used to manufacture sodium and potassium cyanide (see Figure 4.1).

Releases and transfers of 33/50 metals, metal compounds, and cyanide compounds associated with the electroplating process also occur from the production of the inorganic metal salts or other metal compounds (like chromic acid) used in the plating bath. Inorganic chemical manufacturing facilities are classified under SIC 2819 and are required to report their releases in TRI. The 1991 TRI data for releases and transfers of cadmium, chromium, and nickel compounds from SIC 2819 are presented in Table 6.2. Almost 10 million pounds of cadmium, chromium, nickel, and cyanide compounds were released or transferred to the environment from SIC 2819 in 1991. Approximately 96 percent of these releases were chromium compounds released on-site to land-

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electrolyte covers the anode. The stylus is rubbed over the region to be plated (the cathode), which closes the DC circuit.[12] Nickel plating is often done by the brush electroplating method.

Cadmium Plating Baths

The most common method to electroplate cadmium is with an alkaline cyanide bath. Cadmium is supplied to the bath in the form of metallic cadmium or cadmium compounds like cadmium oxide, cadmium cyanide, cadmium sulfate, and cadmium chloride. An all-purpose, bright cadmium bath has a sodium cyanide to cadmium ratio of 5:1, with typical ratios ranging from 4:1 to 7.2:1. Sodium hydroxide and sodium carbonate are also used in the bath solution. Operating temperatures range from 24 to 32°C. For uniform plate thicknesses, a current density of 20 to 40 amperes per square foot (ASF) is typically recommended. However, current densities can range from 5 to 70 ASF, with higher values used for higher speeds and efficiencies.[13] These higher speed operations also require agitation and cooling of the bath.

Cadmium oxide is produced either by the evaporation of cadmium metal and oxidation of the vapor or by the thermal decomposition of cadmium nitrate. Cadmium cyanide is produced by the evaporation of a mixture of dilute cyanic acid and cadmium hydroxide or the precipitation from a solution of cadmium salt and alkali-metal cyanide. Cadmium sulfate is made by melting cadmium metal with ammonia or sodium peroxodisulfate. Cadmium chloride is manufactured by reacting molten cadmium with chlorine gas or vaporizing a solution of cadmium metal and hydrochloric acid. The use of cadmium chloride is declining in industry today, but the salt is still occasionally used in electroplating baths.[14]

Chromium Plating Baths

The equipment and electrolytic solutions used to obtain either a thin and bright, or thick and hard chromium coating are essentially the same. The most common chromium plating bath, known as the conventional or ordinary bath, is a sulfate plating bath with a hexavalent chromium electrolyte. Chromium(VI) is added to the electrolytic solution as chromic trioxide (CrO_3), which forms chromic acid (H_2CrO_4) when dissolved in the aqueous solution. The chromic acid concentration in solution is usually maintained at between 250 to 400 grams per liter (g/l). The sulfate concentration is usually kept constant by adding sulfuric acid or a sulfate salt, with the bath maintained at a chromic acid to sulfate ratio of 100:1 to 125:1.[15] Varying this ratio effects the throwing and covering power, current density, deposition rate, and deposition brightness.

The difference between bright and hard chromium plates lies in the dissimilar solution temperatures, current densities, and plating times. For a bright chromium coating, the operating temperature is kept in the range of 32 to 43°C, the current density is 100 to 200 ASF, and a plating time of 0.5 to 5 minutes is usually sufficient. To obtain a hard coating, an operating temperature of 37 to 65°C is used, the current density can be 150 to 350 ASF and a much longer plating time of 20 to 2,160 minutes is needed.[16]

The chromium(VI) oxide that is used in the chromium plating electrolytic solution is generally produced by an acid reaction. Sulfuric acid is reacted with sodium bichromate, forming a precipitate, which is filtered out of the solution and heated to recover the chromium(VI) oxide. A recently developed process eliminates the use of acid by using an electrochemical cell and sodium dichromate.[17]

Nickel Plating Baths

The three most commonly used nickel electroplating methods are the Watts, all-chloride, and sulfamate baths, though in recent years the use of the all-chloride bath has been limited to more specialized applications.[18] All three methods utilize the same basic inorganic electrolyte compounds - nickel sulfate, nickel chloride, and boric acid - with varying organic additives to effect the plate properties. Organic additives are used to produce the protective, mirror-bright, smooth surfaces required for decorative metal coatings. Pure nickel is used to

based facilities. Like the releases from the primary metals industry or hydrogen and sodium cyanide production facilities, only a fraction of these releases can be attributed to the use of these chemicals in electroplating.

Environmental Releases of 33/50 Metals and Cyanides from Electroplating

Environmental releases of metals, metal compounds, and cyanide compounds that are directly attributed to the electroplating process include releases from job shops classified under SIC 3471 (the plating and polishing industry) and releases from manufacturers who perform electroplating on their own products in captive shops. Releases and transfers of 33/50 metals and cyanide compounds from SIC 3471 reported in the 1991 TRI are presented in Table 6.3. Releases and transfers from manufacturers who perform captive electroplating are listed under the SIC code for the manufacturer's product instead of SIC 3471. No attempt was made to obtain this data from the TRI database since releases from the electroplating process cannot be distinguished from releases from other product manufacturing processes.

On-site releases of chromium compounds to land accounted for almost 73 percent of the total releases and transfers of the 33/50 compounds from the plating and polishing industry. Off-site transfers were also significant. Metal-laced sludges generated as a by-product of the electroplating process are classified under the Resource Conservation and Recovery Act (RCRA) as hazardous wastes.

On-site air releases can result from evaporation of the electrolytic solution and misting from plating tanks. Rinse water is the main source of wastewater from the electroplating process. Other sources of on-site water releases include effluent from treating spent electroplating solution, spills, and solution carry-over. Treatment and disposal of spent plating solutions is a primary source of hazardous waste from electroplating. Off-site transfers include electrolytic sludge from

wastewater treatment and plating tanks. POTWs receive the effluent from wastewater treatment facilities treating plating rinse water.

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

Worker health and safety are a significant concern in the electroplating industry. As discussed previously, hexavalent chromium is classified by EPA as a human carcinogen; cadmium is classified as a probable human carcinogen; nickel dust is classified as a human carcinogen. Cyanide compounds are acute poisons. All of these compounds are toxic chemicals that cause both acute and chronic health effects.

Exposure to cadmium, chromium, and nickel as salts, dust or fumes and cyanides can occur from their use in metal plating and coating. Occupational exposure is a particular problem with chromium plating baths where large quantities of hydrogen are evolved at the cathode and of oxygen at the anode. As the gases break the surface of the bath, they carry bath constituents like chromic acid as a mist. The mists are typically controlled by a tank ventilation system coupled to a scrubber.

OSHA has established occupational exposure limits for cadmium, chromium, nickel, and cyanides. The 8-hour time weighted average PEL is 0.2 milligrams per cubic meter (mg/m^3) for cadmium dust and 0.1 mg/m^3 for cadmium fumes. The PEL established by OSHA for nickel metals and soluble nickel compounds and chromium metal and insoluble chromium salts is 1.0 mg/m^3. OSHA has established a PEL of 5 mg/m^3 for cyanide as the CN moiety.

At least one study has assessed the health status of workers exposed to cyanide fumes and aerosols in a factory during electroplating and case-hardening jobs. The highest levels of cyanide measured in the work environment were 0.8 and 0.2 mg/m^3 in the breathing zone and the general workroom atmosphere, respectively.

TABLE 6.2   RELEASES AND TRANSFERS OF 33/50 CHEMICALS FROM THE INORGANIC CHEMICAL INDUSTRY (SIC 2819)

Chemical	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Cadmium	0	0	0	0	0	0	0	0
Cadmium Compounds	8,966	0	3,746	0	12,712	0	10	10
Chromium	770	0	2,685	0	3,455	0	69,890	69,890
Chromium Compounds	36,944	1,024	9,216,851	0	9,254,819	5,285	146,809	152,094
Cyanide Compounds	28	0	0	0	28	0	0	0
Nickel	1,488	0	250	0	1,738	3,105	250	3,355
Nickel Compounds	53,896	1,640	1,559	5	57,100	12,654	70,932	83,586
TOTAL	102,092	2,664	9,225,091	5	9,329,852	21,044	287,891	308,935

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

The workers complained of typical symptoms of cyanide poisoning like headache, weakness, changes in taste and smell, irritation of throat, abdominal colic, and nervous instability.[23]

Metal compounds can enter the water environment from plating operations when spent plating solutions and rinse water are discarded, and can enter the air by the evaporation and misting of plating solutions.[24] In the past, electroplating shops have been the source of substantial quantities of toxic chemicals in the air and water in industrial areas. In the 1970s, New York City emitted 485 tons per year of chromium. Approximately 43 percent of the daily chromium burden in the New York City sewer system and 24 percent of chromium vapor emissions to New York City air were from electroplating wastes.[25]

EPA has established effluent guidelines and standards for electroplating. The standards limit the concentrations of cyanides, chromium, lead, and nickel that can be discharged in effluent from electroplating facilities. These standards divide electroplating facilities into two categories: facilities that release less than 10,000 gallons per day and facilities that release 10,000 gallons per day or more. The smaller facilities must meet the pretreatment standards for existing sources (PSES) that limit the daily maximum discharge of cyanide amenable to chlorination to 5.0 milligrams per liter (mg/l), of lead to 0.6 mg/l, and of cadmium to 1.2 mg/l. The larger facilities must meet the same effluent standards for cadmium and lead, plus additional standards for nickel (4.1 mg/l), chromium (7.0 mg/l), copper (4.5 mg/l), zinc (4.2 mg/l), total cyanides (1.9 mg/l), and total metals (10.5 mg/l).[26]

EVALUATION OF SUBSTITUTES

Safe substitute approaches to reducing the use of 33/50 metals and cyanide compounds in electroplating include the following:

- product redesign to eliminate unnecessary metal coatings;

- using alternative metal deposition technologies that do not require a plating bath; and

- using safer, less toxic metals or plating bath solutions in the electroplating process.

The first two approaches probably have the greatest potential for reducing the overall environmental releases of 33/50 compounds from metal plating operations, since they eliminate part or all of the metal plating process. Using safer, less toxic metals or plating bath solutions will reduce the adverse health and environmental effects that can result from electroplating, but may not significantly reduce the amount of hazardous waste generated. Most wastewater treatment sludges from electroplating operations are listed as hazardous wastes under RCRA.

In some cases, a product can be redesigned to eliminate the need for a metal plated surface. When product redesign is not feasible, a viable alternative may be a metal deposition technology that does not use a plating bath. Another option is to substitute less toxic metals or plating bath solutions for the 33/50 metals or cyanide-based solutions.

Redesigning the Product

In some instances, the use of metal plating for a component can be eliminated, and it will not adversely affect the part's performance or marketability. Products can be redesigned to eliminate decorative metal plates, use other methods to provide desired coating characteristics, or use substrate materials that do not require plating.

Decorative metal plating is used on all types of products, from the trim on household products to automobile bumpers and interiors. Eliminating the use of metal coatings when they are used for purely decorative reasons would result in an immediate reduction in the generation of hazardous waste. This can be accomplished by using an alternative finish like powder coatings (see Chapter 8) or eliminating the final coating altogether.

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TABLE 6.3   RELEASES AND TRANSFERS OF 33/50 CHEMICALS FROM THE ELECTROPLATING INDUSTRY (SIC 3471)

Chemical	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Cadmium	782	5	0	0	787	258,992	217,114	476,106
Cadmium Compounds	9,248	0	3,747	0	12,995	1,286	54,184	55,470
Chromium	10,604	397	2,935	0	13,936	262,820	732,552	995,372
Chromium Compounds	48,517	1,314	9,228,218	0	9,278,049	20,245	766,487	786,732
Cyanide Compounds	12,838	96	256	0	13,190	20,118	77,684	97,802
Nickel	11,077	1,203	750	0	13,030	274,689	351,674	626,363
Nickel Compounds	63,270	2,355	1,559	55	67,239	28,131	423,848	451,979
TOTALS	156,336	5,370	9,237,465	55	9,399,226	866,281	2,623,543	3,489,824

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

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substrate contact is so intimate that free electron exchange occurs resulting in an atomic weld. The metals that can be mechanically plated must be ductile and include zinc, cadmium, tin, lead, copper, brass, aluminum, silver, indium, and gold.

A unique characteristic of mechanical plating is the ability to easily apply combination, alloy, and layered coatings of two or more metal powders. Plate thickness is not controlled by the length of time the substrate is in the barrel of a mechanical plater, but by the amount of metal powder added to the barrel. Generally, mechanical plating is suited for parts that are normally batch handled, having no greater dimensions than 10 to 12 inches in length, and weighing less than two pounds. Bolts up to 40 inches long have been successfully mechanically plated. Parts with deep recesses or blind holes which trap the glass beads are not usually suited for the process.[30]

Vacuum Metallizing. Vacuum metallizing, which includes vacuum evaporation, sputtering, and ion plating, is another method that applies functional and decorative metal coatings to substrates without the utilization of a bath solution. Vacuum evaporation uses a vacuum chamber in which the parts to be plated are mounted. The pressure in the chamber is reduced to less than one millionth of an atmosphere. The metal to be plated is heated in excess of its boiling temperature to create a vapor pressure considerably higher than the total pressure in the chamber. The metal travels in vapor form into the vacuum chamber and coats the first surface it comes in contact with, i.e., the substrate. The best known and largest used application of vacuum evaporation is the decorative jewelry business where very thin, brilliant films (aluminum) are deposited on plastic or metal substrates.

Sputtering also takes place in a vacuum chamber. In this process a gas plasma discharge is set up between two electrodes, a cathode plating material, and an anode substrate. Positively charged gas ions are attracted to and accelerated into the cathode. The impact knocks off atoms of the cathode, which impact the anode

and thus plate the substrate. Ion plating combines these processes in a third vacuum metallizing application. The substrate to be plated is charged to be the cathode while the coating metal becomes the anode. Vacuum evaporation is limited to a single element, traditionally aluminum; sputtering allows for a wide variety of metals, alloys, and compounds.[31]

Other Metal Deposition Processes. Additional metal deposition processes include chemical vapor deposition and cladding. Chemical vapor deposition is a process for coating a preheated part with the vaporized compounds of metallic salts. The process is also known as gas plating or pyrolitic plating. Cladding is the process of bonding powdered metal or metal sheet to a base metal by a combination of heat and pressure. Cladding is commonly used to produce gold-clad brass jewelry.

Using Safer, Less Toxic Metals and Plating Baths

In many cases, a plating-bath-electroplating process is required to achieve performance or appearance requirements. In these cases, substitute metals or plating bath chemistries can be used to reduce the toxicity of the plating bath and the risk to human health and the environment. Several chemical substitutes have been identified for the 33/50 metals and cyanides used in electroplating. Many of these substitutes, like zinc substitutes for cadmium, have long been recognized as viable substitutes for some applications of the toxic metals.

Cadmium Substitutes. Zinc can be used to replace cadmium in many electroplating applications. Zinc, however, is not as corrosion resistant as cadmium, forms unsightly white corrosion stains, and has poor solderability. A tin-zinc alloy can be used to increase the solderability of the coating and to increase the corrosion resistance. A zinc-nickel alloy has also been tested as an alternative to cadmium plating in marine environments. Preliminary investigations show zinc-nickel affords corrosion protection to steel and ferrous metals in marine environments comparable to that of cadmium.[32]

Metallic-ceramic coatings have also had success replacing plated cadmium in particular applications. The metallic-ceramic coatings, using zinc, aluminum, or alloys of these metals, possess the corrosion resistance characteristic of cadmium, without the environmental issues. Further comparisons of this alternative are presented in Table 6.4. To date, metallic-ceramic coatings have successfully replaced cadmium in more expensive military applications, including landing gear axles of modern aircraft, gas turbine-engine compressor sections, and allied parts.[33] In the future, the positive environmental aspects of this alternative may make it economically feasible in other coating applications.

Cyanide Substitutes. Several non-cyanide plating baths have been developed that can reduce the amount of cyanides released to the environment by cadmium plating. These include the neutral sulfate, acid fluoroborate, and the acid sulfate solutions. These baths have a higher cathode efficiency than the traditional cyanide bath and cause less hydrogen to be generated during the electroplating process. Thus, the danger of hydrogen embrittlement is reduced and the potential for toxic releases to the environment due to misting is reduced. The compositions and

operating conditions for these three alternative baths, compared with a traditional alkaline cyanide bath, are presented in Table 6.5.[34]

In the gold plating process, a sulfate plating bath can be substituted for the cyanide bath. The gold-cyanide solution is the most common method for the plating of gold, especially in the circuit board industry, but it is considered acutely toxic by EPA. A study performed at the Sandia National Laboratories compared the coatings produced on microelectronic circuits by the gold-cyanide and gold-sulfate processes. The test results showed that sulfate gold plating solutions are compatible with a wide variety of substrates used in microelectronic circuits including quartz, aluminum oxide, silicon, glass, cordierite, duroid, and gallium arsenide. Compatibility with surface treatment compounds was also shown in the study. The sulfate bath formed a gold plate that had a similar weld bond strength and produced a coat density that was very close to pure gold. The study concluded that the gold-sulfate bath was much less hazardous than the gold-cyanide bath and produced nearly equal, if not slightly better, coatings.[35] This application is now commercially available.

TABLE 6.4   COMPARISON BETWEEN METALLIC-CERAMIC COATING AND CADMIUM PLATE

	Metallic-Ceramic	Cadmium
Thickness ranges possible	wide range	limited
Size of part	unlimited	limited to tank
Inside/blind holes	can be coated	unlikely
Sacrificial	yes	yes
Potential	0.74 v	0.76 v
Electrical conductivity	yes	yes
Hydrogen embrittlement	no	possible
Temperature of use	> 537°C	limited
Lubrication	requires wax	self-lubricating
Use with paint systems	compatible	compatible

Source:
William B. McCune, "Coatings Without Cadmium," *Machine Design*, July 23, 1993, p. 50, 53

TABLE 6.5   COMPARISON OF NON-CYANIDE CADMIUM ELECTROPLATING BATHS

Bath Component (g/l) or Operating Condition	Alkaline Cyanide	Neutral Sulfate	Acid Fluoborate	Acid Sulfate
Ammonium Chloride	-	11.2 to 22.5	-	-
Ammonium Fluoborate	-	-	59.9	-
Ammonium Sulfate	-	14.9 to 112.3	-	-
Boric Acid	-	-	27.0	-
Cadmium	20.2	3.7 to 11.2	94.4	-
Cadmium Fluoborate	-	-	241.2	-
Cadmium Oxide	22.5	-	-	7.5 to 11.2
Sodium Carbonate	30.0 to 59.9	-	-	-
Sodium Cyanide	101.1	-	-	-
Sodium Hydroxide	14.2	-	-	-
Sulfuric Acid	-	-	-	4.5 to 5.0
Current Density, ASF	5 to 90	2 to 15	30 to 60	10 to 60
Temperature, C	16 to 38	16 to 38	21 to 38	16 to 32

Source:
Metal Finishing 61st Guidebook and Directory, Vol. 91, No. A1, 1993, p. 177

Acid chloride and alkaline non-cyanide electroplating baths can be substituted for the traditional cyanide bath used in zinc electroplating, depending on the substrate to be plated. In general, acid baths are compatible with more substrates, including malleable, high carbon, heat treated, and carburized substrates. These alternative bath solutions are relatively non-toxic to humans, but the acid chloride bath is corrosive to equipment.[36] The Peerless Chain Company of Winona, Minnesota successfully converted their zinc cyanide plating operations, a three-barrel-line and one continuous plating line, to an alkaline zinc plating operation. The loss of intrinsic cleaning qualities of cyanide solutions, the most significant drawback in Peerless' experience, was compensated for by adding an alkaline electrocleaning process prior to plating. One advantage of the alkaline, non-cyanide system was the possibility, after filtration, to reuse treated water back in the plating system.[37]

Electroless plating, also called autocatalytic chemical plating, is an alternative plating technology that eliminates the cyanide bath and the electrical current of traditional electroplating operations. Metal ions in an aqueous solution are chemically reduced (plated) on the catalytic surface of the substrate. The substrate can be a variety of materials (e.g., plastics, metals, and fabric) and is prepared with a thin catalyst film activated by heat or light which, when submerged in the plating solution, initiates the plating process. Metal ions from solution, accepting electrons from reducing agent(s) in solution, are deposited on the catalyzed substrate surface. After the first molecular layer is deposited, the metal then acts as the catalyst to promote further deposition. Metals which can be plated using this technique include nickel, copper, gold, palladium, and cobalt. Solutions chemistries include alkaline and acid baths with various complexing, reducing, and stabilizing agents.[38]

A similar metal deposition process, immersion plating, also uses chemical reduction to accomplish metal plating. However, in immersion plating the reducing agent is the base metal and not a chemical additive. The base

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metal is displaced by another metal ion in solution with a lower oxidation potential than the displaced metal. Deposit-base metal pairs that can utilize this plating technique without a cyanide solution are presented in Table 6.6.[39]

Chromium Substitutes. Less toxic trivalent chromium (Cr(III)) has been shown to be an effective replacement for the hexavalent (Cr(VI)) structure when a thin, bright chromium plating

is required. The coating produced by Cr(III) can vary in appearance from the normal chromium bluish-white to a deep-looking pewter finish, and will not stain if some solution is left on the part. Trivalent chromium can be used for decorative plate and corrosion resistant plating.[40] Due to limitations in plate thicknesses, however, wear-resistant trivalent chromium plate is not possible.

TABLE 6.6   METAL PARINGS FOR NON-CYANIDE IMMERSION PLATING BATHS

Type of Deposit	Base Metal	Bath Ingredients
Bronze	Steel	Stannous Sulfate, Copper Sulfate, and Sulfuric Acid
Cadmium	Aluminum	Cadmium Sulfate and Hydrofluoric Acid
	Copper alloys	Cadmium Oxide and Sodium Hydroxide
	Steel	Cadmium Oxide and Sodium Hydroxide
Copper	Aluminum	Copper Sulfate and Ethylenediamine or Hydrofluoric Acid
	Steel	Copper Sulfate and Sulfuric Acid
	Zinc	Copper Sulfate, Tartaric Acid, and Ammonia
Gold	Copper alloys	Hydrogen Tetrachloroaurate and Ethanol
Nickel	Copper alloys	Nickel Sulfate, Ammonium Nickel Sulfate, and Sodium Thiosulfate
	Steel	Nickel Sulfate
	Zinc	Nickel Sulfate and Sodium Chloride
Silver	Copper alloys	Silver Nitrate, Ammonia, and Sodium Thiosulfate
Tin	Aluminum	Sodium Stannate
	Copper alloys	Stannous Chloride, Thiourea, and Sulfuric Acid
	Steel	Stannous Sulfate and Sulfuric Acid
	Zinc	Stannous Chloride
Zinc	Aluminum	Zinc Oxide and Sodium Hydroxide
	Steel	Zinc Chloride and Ammonium Chloride

Source:
Metal Finishing 60st Guidebook and Directory, Vol. 90, No. A1, 1992, p. 368-372

Besides reduced toxicity, Cr(III) electroplating has a number of advantages over Cr(VI) electroplating. Trivalent chromium has a greater throwing power, covering power, tolerance to current interruptions, and ease of rinsing than Cr(VI).[41] As shown in Table 6.7 the trivalent system also has a lower concentration of chromium than the hexavalent system, which results in less sludge volume upon disposal.[42]

Further, Cr(III) electroplating processes are typically easier than Cr(VI) processes and require less trouble-shooting. Evolution of Cr(VI), which has been identified as a possible drawback to this process, can be significantly controlled by chemical additives or the addition of a secondary anode in solution. The Cr(III) process uses the exact same equipment as the Cr(VI) bath, making it a drop-in replacement.

TABLE 6.7   CHROMIUM PLATING TYPICAL OPERATING CONDITIONS

	Trivalent Chromium	Hexavalent Chromium
Chromium, g/l	5 to 25	100 to 200
pH	2.3 to 4.0	Less than 1
Temperature, °C	70 to 120	32 to 49
Cathode current density, ASF	40 to 150	175 to 300
Agitation	Mid-air	Optional
Rectifier voltage	4 to 15	4 to 12
Anode-cathode ratio	2:1	1:1 to 3:1
Anode material Single-cell Double-cell	Carbon Lead, 7 percent tin	Lead, 7 percent tin
Chromium concentration, g/l Single-cell Double-cell	4 to 20 5 to 10	150 to 300

Maximum thickness, mil
Single-cell
  Room temperature
  High temperature
Double-cell
	about 0.05
	1 or more
	about 0.01
		5 or more

Plating rate, mil per min
Single-cell (constant)
  Room temperature
  High temperature
Double-cell (average)
	0.005 to 0.007
	0.007 to 0.010
	0.004 or less
		0.005 to 0.007

Source:
Metals Finishing 61st Guidebook and Directory, Vol. 91, No. 1A, 1993

A plated tin-cobalt alloy that looks like chromium is another alternative to chromium plating for decorative applications. The process provides a tin-cobalt plate that matches the appearance of bright chromium with a hardness and wear resistance that is sufficient for most indoor, decorative applications. Table 6.8 compares the plate quality and operating parameters of the two electroplating chemistries.

The tin-cobalt plate appearance, ranging from a bright chromium appearance to a warm silvery gray color, is controlled by varying the percent of tin in the metal alloy. The process, either rack or barrel, uses an alkaline sulfate system with optional wetter/amine-based liquid brighteners. To achieve the appearance of a chromium plate, the optimal tin:cobalt ratio in solution, is 50:50. This results in a plate that is 80 percent tin and 20 percent cobalt. Decreasing the cobalt content of the plate below 17 percent results in a mat gray appearance. Additional operating conditions include a pH of around 8.5, and an operating temperature between 38 and 43°C. Current applications of this plating alternative for chromium include automotive interior parts, computer components, bicycle spokes, flexible shower hoses, and screws.[43]

Nickel Substitutes. The versatility of nickel as a metal coating makes it difficult to replace, but the use of nickel can be lowered by using metal alloys. A nickel-iron alloy that contains up to 40 percent iron is used in decorative applications to provide a coating similar in appearance to bright nickel, but without equivalent corrosion resistance. An alloy with 35 percent nickel and 65 percent tin has excellent corrosion resistance. An alloy with 35 percent nickel and 65 percent tin has excellent corrosion resistance, but only retains this property as long as either bronze, copper, or steel is used as an undercoat. The nickel-tin alloy does not have the intrinsic brightness of nickel plate, but it can be mechanically brightened to obtain a similar appearance. Unfortunately, most electroplating alloys are more brittle than their pure counterparts, limiting their versatility.[44]

TABLE 6.8   COMPARISON BETWEEN TIN-COBALT AND DECORATIVE CHROMIUM

	Tin-Cobalt	Chromium
Appearance	Good	Good
Corrosion resistance	Good	Excellent
Wear resistance	Good	Excellent
Tarnish resistance	Good	Excellent
Solderability	Good	Not possible
Metal coverage in recesses	Excellent	Fair
Cathode efficiency	90 to 95 percent	15 to 20 percent
Current density (ASF)	1.9 to 13.9	139.4 to 371.8
Chemical nature	Neutral and non-corrosive	Acidic and corrosive
Barrel production	Conventional barrel plating	Special equipment and slow production

Source:
Tamara Davidson, "Safe, Environmentally Clean Alloy Replaces Chromium," *Design News*, Vol. 46, December 1990

Conclusions

The complexity of electroplating operations and the various plating baths used in the electroplating process makes it difficult to identify across-the-board substitutes. Substitutes are available, however, to reduce the use of the toxic 33/50 metals, metal compounds, and cyanides in many applications. Product redesign to eliminate the use of electroplating is the best environmental alternative, since it eliminates the use of both the metal and the toxic plating bath. Products are already being redesigned in some industries, like the printed circuit board industry, to eliminate electroplating. Decorative electroplating is also being replaced in some industries by paints and coatings.

Metal deposition methods that do not use a plating bath are probably the next choice from an environmental standpoint. These methods eliminate the hazardous plating bath, but not the use of the toxic metal. One drawback to the alternative metal deposition methods is that metal overspray from spraying methods or tailings from remachining thick coatings may actually increase the consumption of metal and the occupational hazards. Thus, alternative metal deposition methods should not be substituted for electroplating without evaluating the potential health and environmental consequences of substitution.

Finally, safe substitutes for the 33/50 metals do exist. Zinc, tin-zinc, tin-cobalt, and other alloys have been shown to be effective substitutes for decorative and some functional applications. An advantage of these alternatives is that many of the bath solutions do not use cyanide. Experimentation and cooperation with vendors and suppliers of electroplating equipment/chemicals is an effective means of identifying alternatives to effectively replace the 33/50 chemicals and metals used in electroplating.

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[32] "Electrodeposited Zinc-Nickel as an Alternative to Cadmium Plating for Aerospace Applications," *NASA Technical Memorandum,* July 1991.

[33] William B. McCune, "Coatings Without Cadmium," *Machine Design,* July 23, 1993.

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CHAPTER 7

PLASTICS AND RESINS

Products made from plastics and resins have become an integral part of modern life. Almost 60.6 billion pounds of plastics and resins were sold by U.S. manufacturers in 1991, down slightly from 61.3 billion pounds in 1990.[1] In 1993, sales figures for plastics and resins increased to more than 68.8 billion pounds for U.S. manufacturers.[2] Assuming that exports and imports are roughly in balance, that equates to more than 200 pounds per year of plastic for every man, woman, and child in the U.S.

> *Since World War II the petrochemicals benzene, toluene, and xylene have been the basic building blocks of plastics and resins. The toxic effects of these 33/50 chemicals and the ever increasing solid waste disposal problem have prompted increased research and development into starch-based and sugar-based degradable plastics.*

The advent of the plastics industry followed World War II, when petroleum supplies were plentiful and the development of products made from petroleum flourished. Today, the 33/50 chemicals benzene, toluene, xylene, and

hydrogen cyanide are among the basic building blocks of the myriad plastics and resins in use. Manufacturers of plastics release large quantities of these chemicals to the environment. Substantial reductions in the use of plastics and resins, by using safe substitutes, could result in an immediate reduction in certain releases of these chemicals. This chapter presents the production, use, and substitutes for products made from polystyrene, one of the many plastic resins made from the 33/50 chemicals.

INDUSTRY PROFILE

Polystyrene is a lightweight material obtained from the polymerization of styrene monomer. The styrene monomer is derived from benzene which is produced by petroleum refining. Polystyrene is used mainly in packaging, disposables, and low-cost consumer goods.

The two common forms of polystyrene are crystalline and foam. Crystalline polystyrene is used to make yogurt and cottage cheese containers, and clear clamshell containers like those used at salad bars. In the foam form, polystyrene is used by the food packaging industry to manufacture cups, bowls, plates,

cafeteria trays, and clamshell containers. Foam polystyrene is also used to package electronics, furniture, and other goods.

Polystyrene is further categorized as molding grade, extrusion grade, or expandable bead grade. Molding grade polystyrene is used in durable or disposable consumer goods. Extrusion grade polystyrene is extruded into foam products or used with a blowing agent to form expandable bead products like popcorn packaging fill.

Polystyrene is a thermoplastic resin. Thermoplastics are characterized by their ability to be cooled and hardened, and then reprocessed when reheated. This ability to be reprocessed makes thermoplastic resins inherently more recyclable than the other general category of plastic resins, thermosetting resins. Thermoplastics represent approximately 87 percent of the plastics and resins sold in the U.S. Other thermoplastic resins include polypropylene, polyvinyl chloride, and polyethylene terephthalate.

Seventeen companies manufactured polystyrene resins at 32 locations in the U.S. in 1992. Table 7.1 lists the producers of polystyrene and their annual production capacities. The following sections discuss the quantities of polystyrene used in the various polystyrene market segments and the price of polystyrene.

Quantity of Polystyrene Used

In 1992 and 1993, polystyrene consumption ranked fifth among the 23 major types of plastic resins produced and marketed in the U.S. Polystyrene consumption ranked behind low density polyethylene, high density polyethylene, polyvinyl chloride and copolymers, and polypropylene and copolymers. Domestic demand for polystyrene was about 5.1 billion pounds in 1993, up from 4.9 billion pounds in 1992. Imports of polystyrene resin amounted to 105 and 137 million pounds for 1992 and 1993,

respectively, while exports were 317 and 340 million pounds for the same years.[3] Both exports and imports are up significantly from 1990 and 1991 figures. The quantities of polystyrene used in 1992 and 1993 in molding grade, extrusion grade, or expandable bead applications are presented in Tables 7.2 through 7.4, respectively.

Consumer demand for the low-cost product markets for which polystyrene is used generally follow the gross national product (GNP). The decrease in polystyrene consumption experienced between 1990 and 1991, however, exceeded the decline expected based on the GNP. Market sources attribute the downturn to environmentally induced cutbacks.[4] A stronger consumer market contributed to the 4.7 percent rise in resin sale between 1992 and 1993.[5]

Price of Polystyrene

Table 7.5 presents the price of polystyrene in crystalline, molding, and expandable bead grades. The prices are before the raw resin is finished or transformed into an application use.

DESIRABLE PROPERTIES OF POLYSTYRENE

The popularity of polystyrene is due, in part, to its ability to be manufactured in crystalline or foam form. Thus, polystyrene can be used in a variety of applications. Either form can be modified with additives to custom make the polystyrene for a particular application. Polystyrene can be made to be fairly chemically inert, protect food products from an oxygen atmosphere, retard food spoilage, and keep food products warm. Polystyrene can also be used to protect durable goods from mechanical damage. Some of the current market development efforts by polystyrene manufacturers are aimed at improving impact strength and surface appearance.[6]

TABLE 7.1   POLYSTYRENE RESIN PRODUCTION CAPACITY

Producer	Location	1992 Capacity (million lbs)
American Polymers, Inc.	Oxford, MA	60
Amoco Corp.	Joliet, IL	210
	Torrance, CA	35
	Willow Springs, IL	70
ARCO Chemical Co.	Monaca, PA	475
ꙍ	Painesville, OH	70
BASF Corp.	South Brunswick, NJ	175
Chevron Corp.	Marietta, OH	480
Dart Container Corp.	Owensboro, KY	66
Deltech	Troy, OH	100
Dow Chemical Co.	Gales Ferry, CT	135
	Ironton, OH	180
	Joliet, IL	235
	Midland, MI	280
	Pevely, MO	130
	Torrance, CA	250
Fina	Carville, LA	640
General Electric Co.	Selkirk, NY	70
Huntsman Chemical Corp.	Belpre, OH	390
	Chesapeake, VA	440
	Peru, IL	255
	Rome, GA	45
Kama Corp.	Hazelton, PA	35
Mobil Oil Corp.	Holyoke, MA	80
	Joliet, IL	480
	Santa Ana, CA	70
Monsanto Chemical Co.	Addyston, OH	160
Novacor Chemical Co.	Decatur, AL	320
	Leominster, MA	120
	Springfield, MA	200
Scott Paper Co.	Fort Worth, TX	90
Tenneco, Inc.	City of Industry, CA	55
TOTAL		6,401

Source:
International Directory of Chemical Producers, 1992: United States of America, SRI International

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TABLE 7.2   POLYSTYRENE USES IN MOLDING GRADE APPLICATIONS

Application	Consumption (million lbs)	
	1992	1993
Appliances/Consumer Electronics		
Air Conditioners	28	30
Refrigerators & Freezers	65	78
Small Appliances	36	40
Cassettes, Reels, etc.	267	290
Radio/TV/Stereo Cabinets	157	176
Other	10	12
Furniture & Furnishings		
Furniture	32	34
Toilet Seats	9	9
Other	11	12
Toys & Recreation		
Toys	123	130
Novelties	46	52
Photographic Equipment	56	63
Other	7	9
Housewares		
Personal Care	74	82
Other	88	96
Building & Construction	50	56
Miscellaneous Consumer & Industrial		
Footwear (heels)	7	7
Medical Equipment	85	95
Other	16	20
Packaging & Disposables		
Closures	96	105
Rigid Packaging	87	96
Produce Baskets	22	27
Tumblers & Glasses	98	96
Flatware, Cutlery	70	90
Dishes, Cups, Bowls	57	63
Blow Molded Items	9	10
Other Injection	103	110
TOTAL MOLDING APPLICATIONS	1,709	1,888

Source:
Modern Plastics, January 1994

TABLE 7.3   POLYSTYRENE USES IN EXTRUSION GRADE APPLICATIONS

Application	Consumption (million lbs)	
	1992	1993
Appliances/Consumer Electronics		
Refrigerators & Freezers	105	109
Other	42	43
Furniture & Furnishings	28	29
Toys & Recreational	39	41
Housewares	61	63
Building & Construction	68	71
Miscellaneous Consumer & Industrial	62	62
Packaging & Disposables		
Oriented Film & Sheet	270	285
Dairy Containers	154	158
Vending & Portion Cups	286	293
Lids	130	136
Plates & Bowls	48	52
Other Extrusion	230	234
Extrusion-Foam		
Board	166	170
Sheet	---	---
Stock Food Trays	200	204
Egg Cartons	52	50
Single-Service Plates	154	160
Hinged Containers	105	108
Cups	50	51
Other Foam Sheet	34	35
TOTAL EXTRUSION APPLICATIONS	2,284	2,354

Source:
Modern Plastics, January 1994

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TABLE 7.4   POLYSTYRENE USES IN EXPANDABLE BEAD GRADE APPLICATIONS

Application	Consumption (million lbs)	
	1992	1993

Billets
    Building & Construction
    Other
	223
	40
		219
		40

Shapes
    Packaging
    Other
	115
	53
		114
		53

Cups & Containers	168	167
Loose Fill	82	82
TOTAL EXPANDABLE BEAD APPLICATIONS	681	675

Source:
Modern Plastics, January, 1994

TABLE 7.5   PRICE OF POLYSTYRENE

Polystyrene Grade	Price ($/lb)
Crystalline	0.40 to 0.41
Molding	0.43 to 0.45
Expandable Bead (packaging)	0.53 to 0.55

Source:
Chemical Marketing Reporter, February 7, 1994

PROCESSES FOR PRODUCING POLYSTYRENE

To obtain styrene monomer, the building block in the polymerization process to obtain polystyrene, benzene and ethylbenzene are required to be sequentially supplied or produced. Chapter 2 presented benzene production processes. The following sections discuss ethylbenzene, styrene, and polystyrene production processes.

Production of Ethylbenzene

Ethylbenzene is produced by the vapor phase alkylation of benzene with ethylene in a fixed bed reactor. In the process, fresh and recycled benzene are preheated, vaporized, and combined with a polyethylbenzene recycle stream and fresh ethylene. The combined feedstock is fed to a reactor that contains a proprietary, fixed, heterogeneous catalyst. The vapor phase alkylation of the benzene with the ethylene occurs at moderate pressures. The effluent from

the reactor is sent to a benzene fractionation system for separation and purification of the ethylbenzene. Unreacted benzene is removed from the first distillation column as an overhead stream and recycled to the reactor. The bottoms stream is fractionated in a two column system.

In the first column, ethylbenzene is separated from higher boiling components and becomes an overhead stream. The bottoms from this column are distilled; polyethylbenzene and other alkylaromatics are recovered in an overhead stream and recycled to the front end of the reactor; the bottoms stream is used as fuel oil. The process is very energy efficient and produces almost no waste heat that cannot be recovered as low or medium pressure steam.[7]

Production of Styrene Monomer

Polymer grade styrene monomer is produced by the dehydrogenation of ethylbenzene. The dehydrogenation reaction uses a commercially available catalyst with a service life of about two years and is carried out in the presence of steam at high temperatures, under a vacuum.

Effluent from the catalytic reactor is condensed and stripped to remove residual aromatics. A subsequent fractionation train separates high purity styrene, unconverted ethylbenzene, and reaction byproducts. Toluene, another 33/50 organic chemical, is one of the byproducts of the reaction. To prevent premature polymerization of the styrene in the fractionation system, a proprietary polymerization inhibitor is added to the system.

Production of Polystyrene

Several processes are used commercially to obtain raw polystyrene, depending on the grade of polystyrene desired and the manufacturer. All of the processes involve the polymerization of the styrene monomer. Two processes performed on a large scale are the bulk and pearl polymerization modes.

Bulk Polymerization Mode. In the bulk polymerization mode, the styrene monomer is continuously polymerized in either the liquid or the vapor state. The type of polystyrene desired for the end-product dictates which reaction conditions are used. Polystyrene resins of high average molecular weight are produced at moderate temperatures without a catalyst. Increasing the temperature and using a catalyst like benzoyl peroxide, oxygen, or stannic chloride causes the average molecular weight of the polystyrene and the solution viscosity to decrease.

Styrene of 99.5 percent purity is typically charged to a stainless steel kettle with other reaction ingredients, heated to 80 to 85°C and polymerized to 35 to 40 percent conversion. The polymerization reaction occurs over 40 to 60 hours. The viscous product solution is then passed down a tower with internal zones of increasing temperature up to 200°C to strip unreacted styrene monomer. The polystyrene is removed in string-like form, cooled and crushed into pellets for end-product manufacturing.[8]

Pearl Polymerization. Pearl polymerization is a batch mode of producing polystyrene, used to prepare special grades of polystyrene. Vessels with 5 to 10 cubic meter (m^3) volume are used to produce spherical polystyrene pellets that are 0.5 mm or smaller in diameter. Addition of low boiling hydrocarbons will yield polystyrene that softens on heating and has very high insulating capacity.[9]

Depending on the grade and formulation of polystyrene required, styrene monomer, water, reaction inhibitors, and suspending agents are added to a batch reactor. The feed mixture is then agitated and subjected to a time-temperature profile. The reaction conditions force the styrene monomer into suspended beads surrounded by the aqueous reaction mixture. Pentane is added to the reactor at a pre-determined time to aid the expansion of the beads. The polymerization reaction continues to nearly 100 percent conversion. The polystyrene beads are then cooled and processed further in a continuous mode.[10]

ENVIRONMENTAL RELEASES FROM PRODUCTION OF POLYSTYRENE

Environmental releases of the toxic chemicals used in the chemical synthesis of polystyrene occur from the production of these chemicals through the styrene manufacturing process. The following sections present the environmental releases of benzene from the benzene production process that can be associated with polystyrene production, and the environmental releases of benzene, ethylbenzene, styrene, and toluene from the production of styrene and polystyrene.

Nearly 100,000 pounds of benzene releases from petroleum refineries can be attributed to styrene production. More than 67,000 pounds of benzene and 2.6 million pounds of toluene were reported released to the environment in 1991 by producers of plastics and resins.

Environmental Releases from Benzene Production

Chapter 2 discussed the environmental releases of benzene from petroleum refineries, where more than 4.9 million pounds of benzene were emitted to the environment. Figure 2.1 showed that about 3.3 percent of crude oil is used as a petrochemical feedstock to produce benzene and other chemical products, including toluene and xylene. Based on the chemical-use tree diagram in Figure 2.3, 53 percent of the benzene feedstock is used to produce ethylbenzene, of which 99 percent is used to manufacture styrene monomer. Using these percentages and a life cycle approach, it is estimated that almost 100,000 pounds of the releases and transfers of benzene from petroleum refineries can be directly associated with benzene's use as a chemical intermediate to produce styrene.

Environmental Releases from Styrene Production

Process air emissions of benzene, ethylbenzene, styrene, and by-product toluene

along the polystyrene chemical synthesis pathway can originate from the intermittent or continuous purging of inert gases from reactor vessels, drying beds, finishing columns, and other process vessels. Fugitive air emissions can result when process fluid leaks from plant equipment such as pumps, compressors, and process valves. Air emissions from storage and handling operations also occur. Other sources of environmental releases or transfers associated with polystyrene production include:

- wastewater discharges directly from the plant into rivers, streams or other bodies of water, or transfers to a POTW;

- on-site release to landfills, surface impoundments, land treatment, or another mode of land disposal;

- disposal of wastes by deep-well injection; and

- transfers of wastes to off-site facilities for treatment, storage, or disposal.

Manufacturers of plastics and resins are classified under SIC 2821 and are required to report their releases in TRI. Table 7.6 presents the environmental releases and transfers of benzene, ethylbenzene, styrene, and toluene that were reported under SIC 2821 in the 1991 TRI. This data are for all plastics and resins manufacturers who reported their releases that year and do not represent the releases just from the production of styrene and styrene products. The data do illustrate, however, the substantial quantities of toxic chemicals that are released to the environment to produce plastics and resins.

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

The health, safety, and environmental issues associated with the use of polystyrene are complex. Benzene, ethylbenzene, toluene, and styrene, the chemicals used or produced during the polystyrene manufacturing process, are all

TABLE 7.6   RELEASES AND TRANSFERS OF CHEMICALS USED TO PRODUCE POLYSTYRENE FROM PLASTIC MATERIALS AND RESINS MANUFACTURING (SIC 2821)

Chemical	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
Benzene	67,274	7	0	0	67,281	0	51	51
Ethylbenzene	142,723	1,405	0	0	144,128	1,029	198,239	199,268
Styrene	2,207,001	1,357	105	0	2,208,463	10,650	800,269	810,919
Toluene	1,522,581	136	20	0	1,522,737	1,703	1,157,579	1,159,282
TOTAL	3,939,579	2,905	125	0	3,942,609	13,382	2,156,138	2,169,520

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

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toxic chemicals with both acute and chronic health effects. Polystyrene products create waste disposal problems since they take up valuable landfill space and do not degrade in the environment. Chapter 2 presented the health, safety, and environmental issues associated with benzene and toluene. The following sections discuss the health, safety, and environmental issues associated with ethylbenzene and styrene and the problems created by the use and disposal of polystyrene.

Ethylbenzene and Styrene

Ethylbenzene may enter the body through inhalation, ingestion, or absorption through the skin. Occupational exposure to ethylbenzene vapors in confined areas has caused collapse, coma, and death. Acute exposure to ethylbenzene by inhalation also causes eye and upper respiratory irritation. Respiratory failure may occur. Prolonged exposure to ethylbenzene vapors may result in nervous system hematological disorders. Ingestion of ethylbenzene may cause transient liver injury.[11] EPA has insufficient data to classify ethylbenzene as to human carcinogenicity (Class D).[12]

Ethylbenzene released to surface water will evaporate fairly rapidly into the atmosphere. When released to soil, it will partially evaporate to the atmosphere, but may also leach into groundwater. Ethylbenzene is degraded in the atmosphere by reaction with photochemically produced hydroxyl radicals. The atmospheric half-life for ethylbenzene ranges from one half hour to two days.[13]

Inhalation of styrene can cause headache, fatigue, weakness, nausea, vomiting, CNS depression, and a sensation of drunkenness. Alterations in psychoneurological functioning have been described from chronic exposure. Styrene exposure irritates the eyes, the respiratory and gastrointestinal tracts, and the skin. Effects on the liver and the reproductive system from exposure to styrene have been reported. The International Agency for Research on Cancer has classified styrene as possibly carcinogenic to humans (Group 2B).[14]

Styrene released to soil will biodegrade, but may also leach into groundwater. Volatilization and biodegradation are the dominant transport and transformation processes for styrene in water. Much of the styrene released into the aquatic and terrestrial environments will partition into the atmosphere. Styrene vapor in the atmosphere reacts rapidly with hydroxyl radicals and ozone. Styrene has been found to be a very active generator of photochemical smog.[15]

Polystyrene

The contribution of plastics like polystyrene to the solid wastestream is an important issue with which many communities are grappling. Diminishing landfill space has prompted an increase in plastics recycling since few plastic materials biodegrade. Even with large-scale recycling, the waste disposal problems associated with the use of plastics are both immediate and long term.

Current projections are for the increased use of polystyrene in all major application markets by 1995. The use of polystyrene and other polymers in the packaging industry results in the nearly immediate placement of the polymer packaging into the municipal solid wastestream. Plastics used in the building industry and other industries that manufacture durable goods are not disposed of for many years. Eventually these polymer products will also require disposal, however, and contribute to the plastics wastestream.

Thus, the percentages of plastics in the solid wastestream is increasing. It has been reported that, in 1991, plastics accounted for four to seven percent by weight (approximately 30 percent by volume) of the solid wastestream.[16] Projections for the year 2000 are that plastics will account for at least ten percent of the stream by weight.[17]

In an effort to dispel the polystyrene waste disposal problem, eight polystyrene manufacturers have formed a coalition called the National Polystyrene Recycling Company

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(NPRC). The company's stated goal is to establish a national recycling program and infrastructure for post-consumer polystyrene products. The NPRC is building five regional polystyrene recycling centers in the U.S. The company claims that through the joint efforts of its members, the technology has been developed to recycle polystyrene on a broad scale. The goal of the company is to see 250 million pounds of polystyrene products recycled annually by 1995. This translates to a 25 percent recycling rate of polystyrene used in food service and beverage packaging.[18]

The types of polystyrene that are slated for recycling include: food trays, hamburger containers, foam cups, protective packaging, single use plates and bowls, meat trays, egg cartons, clear salad containers, and cutlery. Plans are to use the recycled polystyrene to manufacture durable products with a long life span, and not for food service products.

In 1991, the NPRC stated that 20 million pounds of polystyrene were being recycled per year and that each of its recycling centers could handle 13 million pounds per year. The cost for recycled polystyrene pellets in January, 1991 was about $0.26 to $0.40 per pound.[19]

Critics of the NPRC plan point out that even if the NPRC reaches its goal, 75 percent of polystyrene used in food service and beverage packaging and all polystyrene used in other applications will still be discarded. Since polystyrene is a very lightweight material, transporting it to recycling centers may prove to be too costly. Efforts to reduce packaging size, and the widespread use of plastics recycling, may prevent the volume percentage of plastics in the solid wastestream from rapidly increasing. While these efforts are laudable, they do not provide an immediate or complete solution to the plastics waste disposal problem, particularly for products designed to be used once and then thrown away.

Another area of concern with polystyrene products is the use of CFCs and HCFCs as blowing agents to manufacture foam products. The Montreal Protocol and the Clean Air Act

Amendments of 1990 ban most remaining uses of CFCs and HCFCs as foam blowing agents by 1996.

EVALUATION OF SUBSTITUTES

Safe substitute approaches to reducing the use of the 33/50 chemicals benzene and toluene through the reduced use of polystyrene include:

■ eliminating the use of unnecessary packaging;

■ reducing the use of disposable products; and

■ substituting degradable polymers for polystyrene.

Eliminating unnecessary packaging and using reusable durable products are conservation choices that do not require development of new technologies. These safe substitute practices are seeing increased use with increased environmental awareness. The use of unnecessary packaging is already being reduced in some applications, partly because of consumer pressure to market more environmentally friendly products. The use of disposable products can be reduced, particularly in the food industry, by returning to the use of reusable, durable products. Dishes made of glass or reusable dinnerware can, obviously, replace throwaway eating utensils in many applications. Reusable products have some environmental disadvantages, however, like the large amount of energy required to manufacture glass, or to clean products for reuse. Life cycle assessments of plastic versus glass products are being conducted to assess the relative environmental impacts of these materials.

The use of paper products as an alternative to petroleum-based plastic products can also reduce the releases of the 33/50 chemicals. Life cycle assessments of paper versus plastic products are also being conducted.

Degradable plastics, however, are new technological developments for polystyrene

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substitution. They are developed primarily in response to increasing environmental and regulatory pressures. The following sections assess degradable plastics as potential safe substitutes for the polystyrene used in packaging and disposables.

Degradable Plastics Industry

Early in the industrial revolution, virtually all industrial inputs were based on plant and animal products. Paints, varnishes, linoleum, soaps, solvents, and plastics had their origin from plant products, animal products, and/or byproducts of these materials (e.g., methanol). In the last half of the 19th century, several plant-product derived plastics were developed, celluloid being a good example. By the early 1900s, moldable plastics from plants were being used in the manufacture of cars and other consumer goods. In the 1920s and 30s, however, much of the nation's research funding focused on developing plastics and other products from fossil fuels (coal, petroleum, and their derivatives). By the end of World War II, petroleum-based plastics, led by polyvinyl chloride, dominated the plastics market.[20] Faced with limited worldwide reserves of fossil fuels and other environmental concerns in the early 1980s, the focus began to shift again back towards plant- and animal-based plastic products.

Five main categories of degradable plastics have evolved from this new focus: photodegradable plastics, starch-loaded thermoplastics, starch-based plastics, sugar-based plastic; and degradable, petroleum-based polymers. The first two categories; photodegradable plastics and starch-loaded thermoplastics, were developed in the 1980s as a solution to the solid waste problem. However, limitations of these technologies resulted in less-than-desirable solutions.

Photodegradable and Starch-Loaded Polymers. Photodegradable plastics are conventional petroleum-based plastics which contain either carbonyl functional groups or photodegradable additives. These functional groups/additives, when exposed to ultraviolet light, breakdown, thus degrading the plastic. This technology has been used for years in

beverage can rings and waste disposal bags. However, inadequate exposure to ultraviolet light limits the degradability of these plastics within a landfill environment. Starch-loaded thermoplastics use the addition of a degradable filler such as starch to a petroleum-based polymer network. When these products degrade (e.g., dissolution of the starch filler) the polymer network is left behind as small pieces of plastic.[21] Both materials incorporate petroleum-based polymer and do not represent safe substitutes for polystyrene or other petroleum-based plastics within the context of this report.

Degradable, Petroleum-Based Polymers. Degradable, petroleum-based polymers are a new generation of degradable polymers which overcome the limitations of photodegradable and starch-loaded plastics. These products include polycaprolactone (Union Carbide), polyester (Planet Polymer Technologies), and polyvinyl alcohol (Air Products and Chemicals) plastics.[22] Though these materials are fully degradable and offer a potential solution to the solid waste problem, they are still derived from petroleum-based chemicals. Thus, for this report, the degradable, petroleum-based polymers do not represent safe substitutes for polystyrene, and will not be discussed further.

> *Starch-based and sugar-based plastics eliminate the use of benzene and other petrochemicals during their manufacturing processes. Processing characteristics and material properties of these safe substitutes are compatible with many polystyrene products, allowing direct substitution.*

Overview of Starch-Based and Sugar-Based Plastics. The other two categories of polymers, starch-based plastics and sugar-based plastics, also represent the new generation of plastics, but are derived partially or fully from nonpetroleum-based materials. Table 7.7 lists the U.S. producers of these degradable plastics in 1992, their production capacity, and the price of the different plastics. These companies claim

easy processing of their resins in conventional equipment, properties comparable to existing commodity resins, and degradation in soil or water.[22] Base-materials for degradable polymers include starch-based polymers and thermoplastics, polyactic acid and polyactides. Molding, extrusion, and film grade degradable polymers are offered. Manufacturers cite applicability of the degradable polymers to packaging and coatings, mulch bags and other films, and drug delivery systems.

The current focus of the degradable plastics industry is on packaging, specifically plastic bottles, film packaging, and the packaging used in quick service restaurants. In 1993, packaging represented nearly 30 percent of the entire

plastics industry, or nearly 18 billion pounds; polystyrene and polyethylene accounted for about 62 percent of this plastic packaging total. Estimates of present and future market shares of degradable plastics vary. One source states in 1992 degradable polymers comprised 1.8 percent of the total plastics production in the U.S.; in 1993 the percentage had increased to 2.1. This same source estimates by 1996 the degradable plastics share is expected to be more than four percent. Another source states 0.8 percent (or 5 million pounds) of the plastics market is degradable, with a future market of 1.2 billion pounds by 2002. A third source estimates the current global markets for degradable polymers range up to three billion pounds per year.[23]

TABLE 7.7   PRODUCERS OF DEGRADABLE POLYMERS

Producer	Polymer	Capacity (million pounds)	Resin Price $/lb
Cargill	polylactic acid resins	10 (250 by 1996)	1.00 to 3.00
EcoChem	polylactide resins	20 (100 by 1995)	1.50 to 2.00
Ecostar	starch master batch w/ PE copolymer	10	1.30 to 1.60
ICI (now Zeneca)	polyhydroxybutyrate valerate copolymers	1.2 (20 by 1996)	8.50
American Excelsior	Eco-foam (starch)	N/A	$1.30/ft^3$
Novamont	starch w/ copolymer	50	1.60 to 2.50
Novon	starch	100	1.50 - 3.00
UniStar	starch graft copolymer	10 (100 by 1996)	0.75 - 1.25

Sources:
"Biodegradables Blossom Into Field of Dreams for Packagers," *Plastics World*, March 1993, p. 22
"Truly Degradable' Resins Are Now Truly Commercial," *Modern Plastics*, February 1992, p. 62-64
"Bio-Plastics Start to Mature," *Chemical Marketing Reporter*, April 26, 1993, p. 7
"Cargill Moves on Plan to Make Lactic Polymers," *Chemical Marketing Reporter*, May 24, 1993, p. 7
"Now You See It ...," *Chemical Marketing Reporter*, July 6, 1992
N/A: Not Available

Standard Setting for Degradable Plastics.
The American Society of Testing & Materials'
(ASTM) subcommittee on degradable plastics
and the advisory committee of the degradable
polymer project of ASTM's Institute for
Standards Research are developing standard
definitions, classifications, and test procedures
for degradables. The ASTM standards are
intended to provide the basis for substantiating
disposability claims for degradable polymers in
full-scale disposal systems. Sugar-based
degradable polymers will be tested on a number
of solid waste disposal systems, the first of which
will be composting.[24] In the spring of 1993
standard-setting groups from the U.S., Japan,
Germany, and industrial representatives reached
a unanimous consensus that biodegradable
materials must be completely consumed by
microorganisms in a composting process,
producing only natural by-products like carbon
dioxide, methane, water, and biomass.[25]

Other effects are underway to set standards
for degradable plastics and polymers. In April,
1993, the U.S. EPA issued the "Proposed
Degradability Standards for Plastic Ring Holders
for Bottles, Cans" (58 FR 18062). In this
proposal, the EPA sets a guideline for plastic
ring holders to disintegrate within 35 days of
placement in a marine environment. The State
of Florida mandates that materials labeled as
biodegradable do so within 120 days of
placement in a landfill.[26]

Starch-Based Degradable Plastics

Starch-based degradable polymers offer two
main environmental advantages compared to
polystyrene: 1) the use of 33/50 chemicals is
either reduced or eliminated; and 2) the plastics
do not pose a solid waste disposal problem if
managed correctly. Starch-based plastics blend
starches (traditionally corn starch) with
plasticizers and additives to produce a material
that possesses desired plastic properties and can
be thermoprocessed using conventional plastic
processes equipment. Plasticizers are formulated
from various natural and synthetic oils.
Additives include natural and synthetic
compounds, mineral and organometallic salts.

Some plasticizers and additives used in
degradable plastics are readily degradable
themselves and therefore pose limited
environmental risk after decomposition.[27]
However, the U.S. EPA is aware that a number
of additives, in their pure, concentrated form,
are toxic.[28]

Figure 7.1[29] is a schematic of the data in
Table 7.7, showing base materials of some of the
degradable polymers that are currently available.
As can be seen, companies producing starch-
based polymers use a variety of materials, some
of which are petroleum-based. The petroleum-
based polymers used by Novamont, Ecostar, and
UniStar, though degradable, still represent
polymers that use 33/50 chemicals and are not
safe substitutes for polystyrene in the context of
this report. Therefore, further evaluation of
these products will not be performed. Novon
and American Excelsior, however, are two
manufacturers of plastic substitutes that
completely eliminate or greatly minimize the use
of petroleum-based raw materials. Therefore,
this report focuses only on standard plastics made
by these manufacturers as examples of safe
substitutes for polystyrene.

Novon Degradable Polymers. The Novon
Product Group, manufactured by the Warner-
Lambert Company of Morris Plains, New
Jersey, is derived from the renewable resource
of starch from corn and potatoes. The company
claims the polymers have the moldability and
performance characteristics of traditional plastics
with the decomposition benefits of organic
materials like paper. It also claims that all
grades of Novon polymers are completely
degradable in biologically active environments,
like waste treatment plants, and in soil and
water. Exposure to water and naturally
occurring biologically active environments break
down the polymer to water, carbon dioxide, and
naturally occurring minerals that are added
during the polymer synthesis. The mineral
additives are used to vary the properties of the
resin. The polymers can be pigmented and
molded like traditional plastics and have similar
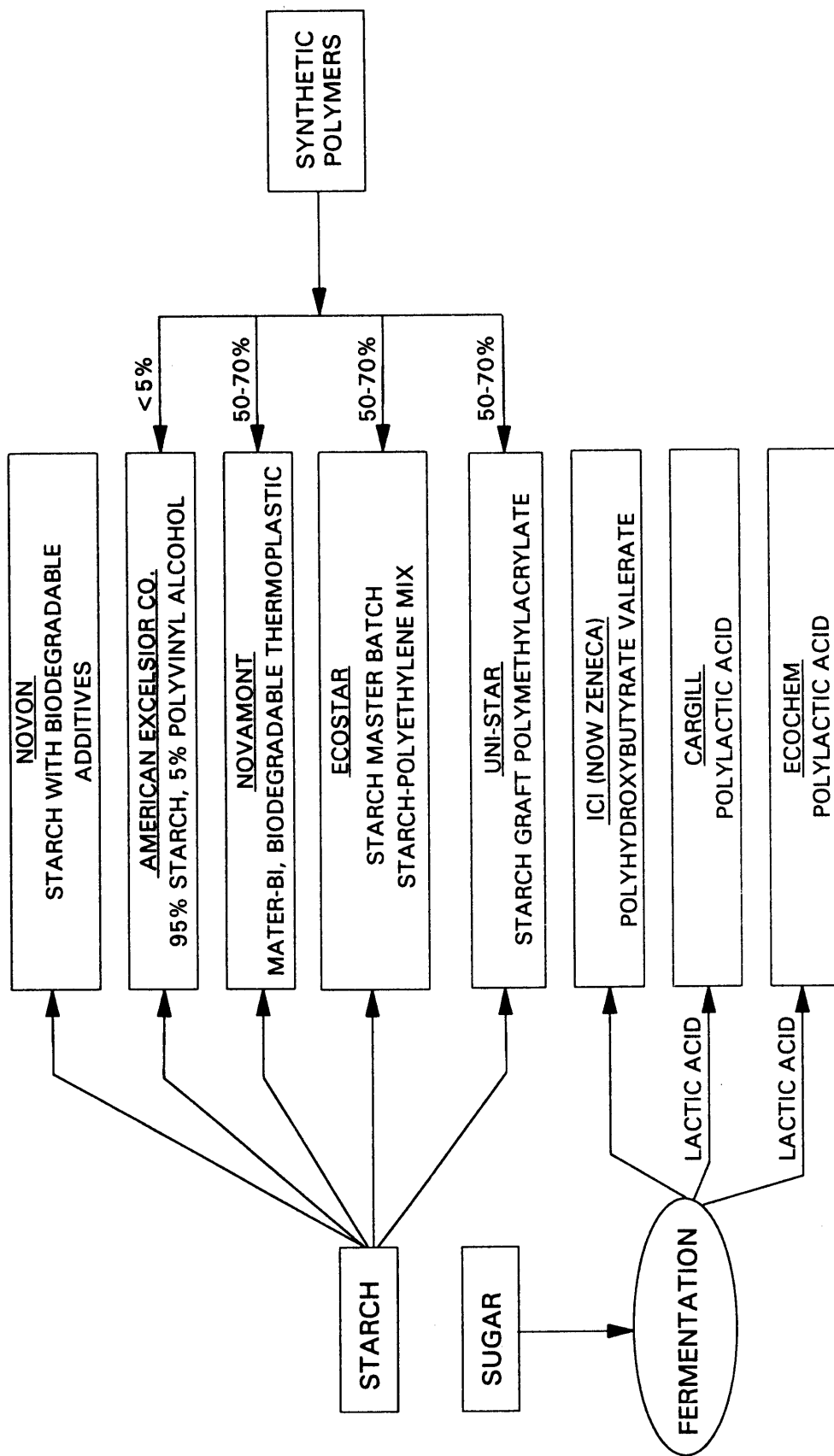strength and appearance.[30]

FIGURE 7.1   RAW MATERIALS FOR DEGRADABLE POLYMERS

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The Novon polymers were first invented in the 1980s by Warner-Lambert for pharmaceutical capsuling applications. The company has 20 experimental grades of Novon polymers in development and started up a 100 million pound per year plant in early 1992 in Rockford, Illinois to produce seven grades of Novon. The Novon 2020 foam grade is intended to replace loose-fill polystyrene peanuts. Novon 3001 grade is an injection molding grade used in applications where quick biodegradation is required. In August of 1993, Novon introduced three new degradable polymers: M4900, an extrudable grade polymer for blown and cast film applications; M5600, a general purpose, injection blow molding; and M1801, a general purpose, injection molding plastic. Possible applications of these plastics include products such as bags (M4900), bottles (M5600), and cutlery and medical products (M1801).[31]

A Cincinnati firm, Storopack, Inc., produces Renature, a product in which the water degradable Novon 2020 is formed into a hollow double tube shape using water as the blowing agent. Storopack claims the performance of Renature is comparable to the polystyrene peanuts used as a packaging agent. After use, the Renature peanuts can be dissolved with water.

Late in 1993 the Warner-Lambert Company announced it would suspend the operations of this Novon Products Group and liquidate its hard assets. Reasons for this announcement included the slow development of the degradable polymers markets and the infrastructure that can handle them, and Warner-Lambert's desire to refocus on the companies core business, pharmaceuticals. No buyer has yet been found.[32]

American Excelsior. The American Excelsior Company of Arlington, Texas also manufactures biodegradable loose-fill peanuts as a safe substitute for polystyrene foam. American Excelsior's product is known as Eco-foam. Eco-foam was developed and patented by National Starch and Chemical Corporation in November, 1990. The company claims that Eco-foam looks, dispenses, and cushions much like expandable polystyrene. When saturated with water,

however, it quickly breaks down into harmless carbon dioxide.

Eco-foam, like the Novon polymer class, is a starch-based material that contains 95 percent corn starch. Unlike the Novon materials, Eco-foam contains a small amount of water soluble synthetic additive (polyvinyl alcohol) which it plans to eliminate from its products in the near future. The product complies with FDA regulations for contact with food but is not a food product. The product is designed to decompose when saturated with water. At exposure to high humidity and high temperatures, the product will shrink but will not become sticky or cling to the package content, thus retaining its packaging properties to a significant extent.[33]

In 1990 Eastman Kodak Company evaluated the use of Eco-foam for packaging a wide variety of products at a Kodak shipping plant in suburban Chicago. Kodak reported that Eco-foam handles and protects very much like expanded polystyrene foam. Kodak found that Eco-foam does not decompose when exposed to normal plant humidity levels and offers the same flowability and cushioning ability as expandable polystyrene. Since that time Kodak, Sony, and Canon, among others, have switched to Eco-foam as a drop-in replacement for polystyrene peanuts.[34] In 1990 starch-based loosefill packaging didn't exist; now it constitutes ten percent of a 55 million pound annual market.[35]

The major drawback to Eco-foam is its cost, about one-and-a-half to two-times the price per pound of traditional loose-fill materials. Cost is expected to decrease as capacity and demand for the product increases. American Excelsior is investing $400,000 in equipment at six U.S. plants to expand production nationally.

Sugar-Based Degradable Polymers

Two naturally degradable polymers, derived from the fermentation products of starches and sugars, are also potential substitutes for polystyrene and other petroleum-based polymers (Figure 7.1 again). One naturally degradable polymer, marketed by Zeneca (formerly ICI), is poly(hydroxybutyrate valerate) (PHBV). This polymer is produced by the fermentation of plant

sugars (glucose) and simple organic acids. Varying the amount of organic acid in the fermentation process varies the valeric content of the polymer, thus controlling the physical properties of the product; the more valeric content of the polymer, the more flexible and ductible the final product is. PHBV is more moisture resistant than starch-based products, and also resists oils and greases. PHBV's lower melting temperature and viscosity will require setting changes in the processing equipment currently used with polyethylene (the plastic PHBV is suited to replace). This material is already commercialized in Europe under the trade name Biopol, and is used in shampoo bottles, disposable razors, and writing pens.[36]

Another naturally degradable polymer is polylactic acid (PLA). PLA is also derived from the fermentation process of starch-based materials which produces "natural" lactic acid synthetic (lactic acid can also be manufactured from petrochemcials, hence the "natural" notation). Lactic acid is then fed into a proprietary polymerization process to produce PLA. Currently, the major manufacturers of lactic acid/PLA are Cargill and EcoChem. Cargill's $8,000,000, ten million pound per year lactic acid/PLA facility in Savage, Minnesota became operational in February, 1994. Officials of Cargill predict that by 1996 market demands will require a larger facility with a capacity of 250 million pounds per year. The source of starch for Cargill is corn processing by-products. EcoChem's Adell, Wisconsin facility (20 million pounds per year capacity) began operations in 1992. They have plans to expand this facility to produce 100 pounds per year of PLA by 1995. Cheese whey is EcoChem's starch source.[38]

PLA is clear and not readily soluble in water. Although not as well established in the commercial market as PHBV, expected applications include disposable food containers, cutlery, diapers, personal hygiene products, medical garments, yard bags, and agricultural applications.[39]

Management of Degradable Polymers

Two of the driving forces behind the development of degradable polymers were the issues of solid waste and the increasingly scarce space available in landfills. It was estimated that packaging waste accounted for nearly 30 percent by volume of the municipal solid wastestream in 1991.[40] Degradable polymers were initially marketed as a solution to these issues. Modern landfills, however, are not designed and managed to allow degradation, even of readily degradable materials; they are designed to minimize moisture and heat to control methane gas build-up and minimize the potential for groundwater contamination.[41]

Current manufacturers of starch-based and inherently degradable polymers realize this limitation of landfills; even degradable plastics constitute a landfill disposal problem. The new degradable plastics producers, therefore, de-emphasize the need to fit into traditional disposal methods (i.e., landfills and incineration). They support the further development of a compost infrastructure to properly manage their products. Composting optimizes the environmental conditions (biological activity, heat, and moisture) needed to facilitate degradation of materials to CO_2, water, and mineral-rich soils. When properly disposed of in compost facilities, starch-based, PHBV, and PLA plastics reportedly decompose within 60 to 120 days.[42]

To date, there are 19 mixed municipal solid waste composting facilities in the U.S., with 7.5 million pounds per day processing capabilities. Nine more facilities are under construction and 33 others are in various stages of planning. Even with these existing and planned facilities, the infrastructure to properly manage the 40 percent of municipal solid waste which is compostable (including degradable plastics) is not adequate.[43] Without such an infrastructure, the extent to which degradable polymers can enter the market may be limited.

Research is also needed on the mechanisms of degradation and the environmental characteristics of degradable plastics and their degradation by-products in a compost environment. To address these issues a new industrial research consortium was formed in February, 1993. Cargill, Novon, EcoChem, Minnesota Corn Growers, Philip Environmental, a Canadian resource recovery firm, and Michigan State University, with funding from the U.S. Department of Agriculture, have begun a two-year compost demonstration project. The project will look at the biological and chemical activities that degrade the variety of materials that enter a composting facility, and the toxic/environmental characteristics of the byproducts.[44]

Finally, research is needed to investigate the environmental impacts of other options for managing discarded degradable polymers. For example, many of the starch-based plastics will quickly dissolve in water. Assuming the proper industrial discharge permits have been obtained, industrial users of degradable polymers could dissolve them in water and discharge the effluent to a local POTW. Similarly, individuals who purchase products packed in starch-based, loose-fill "peanuts" could dissolve the packaging and discharge it to the local sewer system. With a

large-scale switch to degradable polymers, however, research is needed to determine the effects of the resulting increase in biological oxygen demand on local POTW capacity.

Conclusions

The use of polystyrene can be reduced through the use of substitutes, reducing the use and releases of benzene and other 33/50 chemicals and helping alleviate the nation's solid waste disposal problems. Conservation choices like eliminating unnecessary packaging and using reusable products or using safe substitutes like degradable polymers are practical, viable ways to reduce the use of polystyrene. Already, polystyrene use-reduction is occurring as environmentally conscious consumers encourage manufacturers to use less packaging or environmentally sound materials. These safe substitute approaches help diminish the amount of plastics in the nation's solid wastestream and reduce the nation's hazardous waste burden by reducing the use of toxic chemicals. Further information is needed, however, on synthetic additives used in some degradable polymers to verify that these additives do not cause adverse human health or environmental effects.

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CHAPTER 8

PAINTS AND COATINGS

The product class of paints and coatings includes paints, varnishes, lacquers, and other materials that form a solid, cohesive, and well-adhering film when spread over a surface in a thin layer. Paints and coatings are used to decorate and protect a substrate like metal, wood, or plastic from air, microorganisms, water, and chemicals. They may also provide improved mechanical properties like better hardness and abrasion resistance. The consistency and film properties of a paint or coating are usually developed for a limited field of application and a particular coating process.

Traditionally, paints and coatings have been solvent-borne liquids using 33/50 chemicals (toluene, xylene, MEK, and MIBK) as solvents or diluents. With increased concern over the health and environmental effects of solvent releases, however, safe substitutes for solvent-borne coatings are seeing increased use. This chapter describes the use of and safe substitutes for 33/50 organic solvents in paints and coatings.

INDUSTRY PROFILE

The paints and coatings industry consists of two sectors: trade sales or shelf goods and chemical coatings or industrial product finishes.

Trade sales or shelf goods include architectural paints sold to consumers, contractors, or professional painters for use on new construction or for maintenance. They are usually air-dry finishes which do not require baking or some other physical process after application.

Chemical coatings or industrial-product finishes are used in factory applications to coat consumer products such as automobiles and appliances. These finishes are produced to manufacturers' specifications and are usually applied on a production line and then baked. These paints are traditionally applied by spray, dip, roller, or electrodeposition.

> *The 33/50 chemicals toluene, xylene, MEK, and MIBK are widely used as solvents or diluents in solvent-borne paints and coatings. With increased concern about the health and environmental effects of solvent releases, however, safe substitutes for solvent-borne coatings are gaining in market share.*

The industrial paints and coatings market in the U.S. in 1990 was about $7.2 billion, while the trade sales market was approximately $4.6 billion. Although not the largest market segment

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in terms of expenditures, the trade sales sector is the largest segment of the paints and coatings market in terms of volume.[1]

Paints and coatings can be classified according to their use (e.g., automotive, marine, architectural), application method (e.g., spray, dip), processing state (e.g., water-based, solvent-borne), drying behavior (e.g., cold curing, air-dried, heat-cured), or chemical nature of the binder (e.g., alkyd resin, epoxy resin). Usually, more than one of these parameters is required to specifically define and characterize a coating system. One of the more common classifications, however, is based on binder chemistry, which is indicative of the working properties of the coating material and performance of the film. Paints and coatings classified according to the types of resins or binders present include oil-based coatings, cellulose-based coatings, vinyl coatings, acrylic coatings, alkyd coatings, saturated or unsaturated polyester coatings, polyurethane coatings, epoxy coatings, and asphalt, bitumen, and pitch coatings. Some resins in a class may be soluble in organic solvents, while other resins in the same class are soluble in water or are water dispersible.[2] Toluene, xylene, MEK, and MIBK are used as solvents or diluents for a number of the different resins used as binders.

Quantity of 33/50 Organic Solvents used in Paints and Coatings

Table 8.1 presents the quantity of 33/50 organic solvents used in paint and coating formulations between 1979 and 1989. The total consumption of all of the major solvents used in paints and coatings during this period is also shown for reference.

Increasingly stringent environmental regulations have caused industry to decrease the concentration of solvents in paints and coatings. The production of conventional solvent-based coatings has dropped from about 100 million dry gallons in 1983 to about 65 million dry gallons in 1987. On the other hand, production of high-solids (i.e., lower solvent concentration) solvent-based paints increased from 18 million dry

gallons in 1983 to 35 million dry gallons in 1993.[3]

The trend toward decreased production of conventional solvent-based paints does not agree with the solvent consumption data in Table 8.1. These data show that overall solvent use in paints and coatings has actually experienced a steady, though small, increase since 1982. No explanation was found in this study for the increase in consumption of solvents in paints during a period when solvent-borne paint consumption was declining.

Price of 33/50 Organic Solvents in Paints and Coatings

Table 2.5 in Chapter 2 listed the prices of the 33/50 organic solvents that are used in paints and coatings. Prices range from $0.67 per pound for toluene to $0.23 per pound for o-xylene. The price of the 33/50 aromatic organic solvents are dependent on the price of crude oil and market demands for other petroleum products.

Traditional solvent-based paints contain 50 to 70 percent solvents. Although the solvent is the single largest component of a solvent-based paint or coating formulation, it contributes a smaller fraction of the cost.

COMPONENTS OF PAINTS AND COATINGS

The three major components of solvent-borne paints are pigments, binders, and solvents or thinners. A number of additives, such as driers, anti-skinning and anti-settling agents, and fungicides or bactericides, are also used.

Pigments

Pigments and extender pigments offer paints and coatings their color and hiding power, as well as increased resistance against corrosion and wear in certain cases. Pigments consist of metal, inorganic, organic, and organometallic compounds dispersed in the paint and film.[4] The type of pigment determines the color and color stability of the paint or coating, while the amount

TABLE 8.1   ESTIMATED CONSUMPTION OF 33/50 ORGANIC SOLVENTS IN PAINTS AND COATINGS

| Solvent | Estimated Consumption (million lbs) Year | | | | | | | | | | |
	1979	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989
Methyl Ethyl Ketone	367	340	310	290	310	320	335	335	340	315	300
Methyl Isobutyl Ketone	112	105	100	90	100	106	110	110	110	118	119
Toluene	675	585	580	550	580	600	610	610	615	635	640
Xylenes	515	470	465	410	440	455	465	465	465	475	480
TOTAL 33/50 ORGANIC SOLVENTS	1,669	1,500	1,455	1,340	1,430	1,481	1,520	1,520	1,530	1,543	1,544
% Change 33/50 Organic Solvents[a]	N/A	-10.1	-3.0	-7.9	+6.7	+3.6	+2.6	0.0	+0.7	+0.8	+0.1
TOTAL (ALL ORGANIC SOLVENTS)	4,503	4,139	4,041	3,704	3,995	4,184	4,249	4,222	4,283	4,345	4,349
% Change (All Organic Solvents)[b]	-1.3	-9.3	-2.4	-8.3	+7.9	+4.2	+2.0	-0.6	+1.4	+1.5	+0.1

Source:
1991 Directory of Chemical Producers, United States of America, SRI International
[a] Net change between 1979 and 1989 for 33/50 organic solvents was -7.5 percent
[b] Net change between 1979 and 1989 for all organic solvents was -5.1 percent
N/A: Not Available

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of pigment determines the gloss, hiding power, and permeability of the coating. The degree to which the pigment is dispersed in the binder, and the volume of film occupied by the pigment also influence the film properties. A gloss paint contains enough binder so that all pigment particles are completely encased, giving a smooth glossy surface. In a flat paint, particles of the pigment which are not covered by the binder protrude at the surface, breaking up reflected light and producing a dull surface.

Binders

Binders of paints and coatings, which include film-forming substances and plasticizers, constitute the continuous phase in paint films and contribute to the films protective and general mechanical properties. Important properties of the film include flexibility, durability, and chemical resistance. Film-forming binders can be either macromolecular products (large, intricate molecular structures) or low-molecular-mass polymers that react to form macromolecules on curing. Macromolecules include cellulose nitrate and vinyl chloride copolymers; low-molecular-mass polymers include polyurethanes and epoxy resins. Most film-forming binders are resins (e.g., alkyl resins, epoxy resins). Resins are readily soluble in either organic solvents or water, but not both. They increase film hardness and reduce the drying time in oxidative curing systems. Plasticizers, also identified as binders, are most often organic liquids of low volatility (e.g., esters of poly acids). They have the opposite effect to resins on the final coating; they improve the flexibility of the formed film. Binders are usually organic materials, but a few inorganic binders are used.

Solvents

Solvents or thinners are usually volatile organic liquids. They dissolve binder components and provide a means of adjusting the viscosity of the solution for processing consistency. Solvents also improve the wetting capabilities of the solution, dispersion of the pigments, and leveling and gloss of the film.[5]

Following application, the vast majority of the solvent is lost during the film formation process and does not influence the performance of the dry film. Solvents are also used as diluents to reduce the cost and assist in the solution of other ingredients.

Toluene is the most extensively used diluent for cellulose nitrate lacquers. It will also dissolve a large number of resins, but is not a solvent for PVC, copals, or shellac. Toluene is miscible with drying oils like linseed oil or tung oil used in oil-based paints and with most other solvents.[6]

Xylene has high solvent power for a wide range of resins and a high rate of evaporation. As a result, xylene is widely used in both stoving (heat-cured) and rapid air-drying coatings. Like toluene, xylene is used as a diluent for cellulose nitrate lacquers. It is the main solvent for lacquers made with polystyrene, polymethlymethacrylate, and chlorinated rubber binders. Xylene is also an excellent solvent for asphaltic bitumen and petroleum pitch.[7]

MEK and MIBK are solvents for a wide range of resins. MIBK is extensively used in both stoving enamels and lacquers.[8]

Until the early 1980s, paints usually contained 50 to 70 percent solvents by volume. Since then, high-solids paints and water-borne systems have replaced many traditional coating materials in industry, handicrafts, and households. Still, except for powder coatings and a few other solvent-free paints, organic solvents are used in all paints, even those that are water-borne.[9]

DESIRED PROPERTIES OF PAINT AND COATING SOLVENTS

Solvents are used in paints and coatings to reduce the viscosity of the material and thus facilitate the application of a uniform coating. Solvents are also used to disperse pigments and extenders. Solvents used in a particular paint or coating must be suitable for the oil or resin present. The important properties of paint solvents are: 1) solvent power; 2) rate of evaporation; 3) boiling point and distillation

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range; 4) flash point and inflammability; and 5) toxicity.[10] A solvent is typically selected based on its ability to dissolve a resin and its evaporation rate.[11] Solvent combinations are often used in paint formulations. Therefore, the changes in the solvency of the resins as the different solvent components evaporate must also be considered.

Classes of materials used as organic solvents include aliphatic hydrocarbons, aromatic hydrocarbons (toluene, xylene, and the trimethyl benzenes), ketones (MEK, MIBK), alcohols, esters, and glycols esters.

COATING PROCESSES

Solvent-borne paints and coatings may be applied to a surface in a number of ways. Architectural or trade-sales paints are applied by brush or hand roller, but may be sprayed by professional painters on large exterior surfaces. Industrial coatings are applied on a production line using one of a number of processes and then cured, usually by an accelerated curing operation. Coating processes used for solvent-borne trade-sales paints do not differ significantly from those used for other liquid paints like water-borne coatings. The coating processes in industrial applications can, however, differ significantly, since the coating may be in liquid or solid form. Typical processes for applying solvent-borne (liquid) industrial coatings and the film formation process are discussed briefly below.

Dip, Flow, Curtain, Roller, and Coil Coating

Dip coating includes hand-dipping, automatic dipping, rotational dipping, and other methods for dipping articles in a tank filled with a paint or coating. Flow coating is a variation of dip coating where the paint is either allowed to flow over the objects or the paint is directed at the objects from nozzles. Curtain coating is, in effect, a variation of flow coating used for large, flat panels, which may have raised moldings. The panels are carried on a conveyor through a curtain of paint that flows from a pressure head.

With roller coating, paint is applied by transfer from rollers to one or both sides of flat materials. Coil coating, a variation of roller coating, is used to coat metals in the form of a continuous strip.

Spray Coating Methods

There are numerous spray methods for applying paints and coatings, including the conventional air-assisted, hot-airless, electrostatic, and combination methods. In general, spray methods use specially designed spray guns to atomize the paint into a fine spray, which is directed at the object to be painted.

For industrial applications, the paint is typically contained in a pressure vessel and fed to the spray gun using compressed air. Air-spray processes have a certain amount of overspray and rebound from the sprayed surface, which results in paint-laden air. Application efficiencies are as low as 20 percent for conventional air-spray processes.[12] Spray booths with an open front and exhaust at the rear are used to remove the overspray as it is generated.

In hot-airless applications, the paint is heated to reduce its viscosity, which allows paints with higher solids content (i.e., less solvent) to be used. Fluid pressure at the gun orifice is used in airless spray applications so that the pressure drop at the nozzle, when the paint is released, will atomize the paint. Airless spray guns have reduced overspray and rebound and have higher application rates.

Electrostatic spray guns are based on the principle that negatively charged objects are attracted to positively charged objects. The article to be painted is usually attached to a grounded conveyor. A system of electrodes or wires are used to create an electrostatic field between the electrodes and the article. Atomized paint from a conventional spray gun is injected into the field where it acquires a negative charge and is attracted to the grounded article. Electrostatic spray systems are very efficient (application efficiencies as high as 90 percent) and have low operating costs. The initial capital investment, however, is high, and careful control of the solvent concentration is required.[13]

Film Formation

The film formation process is the transformation of the applied coating into a solid film that adheres tightly to the substrate. The quality and characteristics of the final film depend on the composition of the paint, the nature and pretreatment of the substrate, and the processing conditions of application and film formation.

Physical drying and chemical drying are the two general routes of film formation. Physical drying paints and coatings rely on the evaporation of the carrying agent (e.g., solvent, water) from the applied coating (polymer solution or dispersion) to create a solid film. These paints are characterized by a low solids content due to the low solubility of the thermoplastic polymers. Binders of physically drying paints and coatings include cellulose esters, vinyl resins, thermoplastic acrylic resins, and polyurethanes. All physically dried coatings are sensitive to solvents that swell or dissolve them.[14]

Chemical drying paints and coatings create a film by the cross-linking of the binder through oxidative reactions (absorption of oxygen to form ether bridges). The oxidative reactions can be initiated by heat, surface catalysts, or radiation (e.g., infrared, ultraviolet). Characterized by a high-solids content, chemically drying paints and coatings employ polyester, epoxy, alkyd, vinyl, and acrylic resins in conjunction with cross-linking agents such as phenolic and amino resins and isocyanates.[15]

ENVIRONMENTAL RELEASES OF 33/50 ORGANIC SOLVENTS FROM THE PAINTS AND COATINGS INDUSTRY

Environmental releases from the use of 33/50 organic solvents in the paints and coatings industry occur from the chemical manufacturing process through the application of paints and coatings to the final disposal of paint residuals. The following sections present environmental releases of organic solvents from the production and distribution of paints and coatings and estimates of releases from with their application.

Environmental Releases from Production

Releases and transfers of the 33/50 organic chemicals from their production facilities reported in the 1991 TRI were discussed in Chapter 2. By using a life cycle approach, a significant fraction of the releases of MEK and MIBK from production facilities can be associated with the paints and coatings industry, since it is the largest end-use for these chemicals. Since toluene and xylene consumption in paints and coatings is small compared to other uses for these chemicals, a much smaller fraction of the losses of toluene and xylene from petroleum refineries can be attributed to the paints and coatings end-use. Again, using a life cycle approach, some of the toluene, xylene, MEK, and MIBK losses from distribution facilities are associated with their distribution to paints and allied products manufacturers (SIC 2851). Distribution facilities are not currently required to report releases and transfers in the TRI.

The 1991 releases and transfers of toluene, mixed xylenes, o-xylene, MEK, and MIBK from paints and allied products manufacturers reported in the TRI are shown on Table 8.2. Almost 7.5 million pounds of these chemicals were released on-site to the environment (mainly to air) from paints and allied product manufacturing facilities alone. Another 4.8 million pounds were transferred to off-site treatment or disposal facilities. By using safe substitutes with reduced or eliminated 33/50 organics, these on-site releases to the environment and off-site transfers of the toxic 33/50 organics could be reduced or eliminated.

Environmental Releases from the Paints and Coatings Process

Emissions of volatile organic air pollutants occur from the application of solvent-borne paints or coatings. At large industrial facilities these emissions are typically controlled by use of add-on control devices that either destroy or collect the organic solvents for reuse or disposal.

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TABLE 8.2 RELEASES AND TRANSFERS OF 33/50 ORGANIC COMPOUNDS FROM THE PAINTS AND ALLIED PRODUCTS INDUSTRY (SIC 2851)

Chemical	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfer
MEK	2,118,118	35	755	0	2,118,408	15,696	979,587	995,283
MIBK	555,424	4	255	0	555,683	294	414,497	414,791
Xylenes (Mixed isomers)	2,402,488	1,015	6,115	1	2,409,619	70,452	1,599,904	1,670,356
o-Xylenes	1,237	0	0	0	1,237	0	1,500	1,500
m-Xylene	8,014	0	0	0	8,014	0	40,738	40,738
p-Xylene	1,500	0	0	0	1,500	0	0	0
Toluene	2,346,044	529	505	0	2,347,078	81,093	1,618,214	1,699,307
TOTAL	7,432,825	1,583	7,630	1	7,442,039	167,535	4,654,440	4,821,975

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

The principal control devices are catalytic and noncatalytic incinerators, activated carbon or other types of absorbers, liquid scrubbers, or refrigerated condensers.

Even with control devices, substantial releases of organic solvents occur from industrial paint and coating production lines. In addition, smaller facilities like automobile repair shops may not use control devices. Further, pollutants are usually allowed to evaporate directly to the atmosphere during consumer application of trade-sales paints.

No attempt was made to obtain the releases and transfers of the 33/50 organic chemicals from industrial paints and coatings processes from the 1991 TRI, since this use is spread across numerous industry groups. However, EPA has developed air emission factors for solvent losses from paints and coatings applications. EPA estimates that all toluene and 87 percent of the xylene isomers used in paints and coatings are emitted to the atmosphere when the emissions are uncontrolled.[16] No emission factors are available for MEK and MIBK used in paints and coatings, but it can be assumed that, like toluene and xylene, virtually all these solvents are eventually released to the atmosphere. Applying these uncontrolled emission factors to the estimated consumption of 33/50 organic solvents in paints and coatings (see Table 8.1), 1.5 billion pounds of 33/50 organic chemicals could have been released to the environment from paints and coatings in 1989. The actual amount was likely much smaller due to controls on larger sources.

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

The manufacturing and use of solvent-based paints and coatings result in a number of health and environmental concerns. Areas that have a number of paint-consuming industries may have an appreciable amount of atmospheric pollution by organic solvents.[17] These problems have prompted a number of states to promulgate regulations to control releases of VOCs from

paints and coatings. The 33/50 chemicals used as solvents in paints and coatings are all VOCs which degrade in the atmosphere and contribute to photochemical smog formation. State or local regulations typically impose limits on the concentrations of solvents in paints and coatings, or on release rates from the industrial consumption of paints and coatings. In addition, EPA established a number of New Source Performance Standards (NSPS) for several types of surface-coatings lines in the 1980s. The NSPS establish maximum allowable emission rates of VOCs based on the volume of paint or coating consumed.

> *When a consumer paints the interior or exterior of a house or other surfaces, the solvents evaporate directly to the atmosphere as the paint dries. This and industrial uses of paints and coatings result in the environmental release of several hundred million pounds of the 33/50 organics each year.*

Under Clean Air Act scheduling, VOC regulations for architectural and industrial maintenance paints and coatings were due by the end of 1993. These regulations will require VOC emissions in 1996 to be at least 15 percent below 1990 levels in ozone non-attainment areas.[18] Other requirements of the proposed regulations include a 25 percent reduction (from 1990 figures) in VOCs for all paints, excluding specialty paints, by 1996 and a 45 percent reduction by 2003.[19]

Despite state or federal regulations and the use of control technologies in industrial processes, there are still substantial releases of organic solvents from paints and coatings. In addition, it is difficult to prevent inhalation of solvent vapor by workers during the production and use of paints and coatings.[20] Studies of the neurotoxic effects found in workers in industrial paint and coating applications have described symptoms like fatigue, difficulty in concentrating, and short-term memory loss. These symptoms have not been observed in

painters in the architectural sector who mainly use water-borne paints.[21]

Consumers who use solvent-borne paints may be most at risk from inhalation of toxic vapors, since the average consumer probably does not wear respiratory protection and has inadequate ventilation in the indoor work area. Further, household disposal of trade-sales paint residues represents a large and poorly documented part of the nation's hazardous wastestream. Thus, use of safe substitute technologies by industry and alternative formulations by consumers would substantially reduce the nation's hazardous waste burden and the release of toxic air pollutants.

EVALUATION OF SUBSTITUTES

The increasingly stringent government regulations affecting the paints and coatings industry and cost of compliance have spurred the development of a number of safe substitutes for solvent-borne paints and coatings. These safe substitutes include the following:

■ product redesign to eliminate unnecessary paints and coatings;

■ water-borne paints;

■ liquid high-solids paints;

■ aqueous dispersions; and

■ powder coatings.

Where applicable, these safe substitutes are quickly gaining acceptance in both the consumer and industrial sectors. In 1993, one source estimated water-borne paints represented 15 percent of the entire paints and coatings market (including original equipment manufacturing (OEM), industrial coatings, and architectural coatings sectors), liquid high-solids paints represented 11 percent, and powder coatings two percent.[22] Another source placed the market share for water-borne paints and coatings even higher: nearly 20 percent of the OEM coatings

sector, more than 55 percent of the architectural coatings sector, and 18 percent of the industrial coatings sector.[23]

Product Redesign

Paints and coatings are applied to a substrate to improve its appearance or provide an engineering function. Many manufacturers are finding that they can eliminate unnecessary paints and coatings used only for appearance purposes. Not only does this reduce capital, operating, and maintenance costs, it also reduces their potential liability from toxic chemical use. Furthermore, the elimination of unnecessary paints and coatings has ramifications beyond the reduction in use of the 33/50 chemicals used as carrying solvents. It also reduces the use of the following:

■ inorganic pigments made from the 33/50 metals;

■ organic pigments made from the 33/50 aromatics;

■ resins (binders) made from the 33/50 aromatics and cyanides;

■ additives such as plasticizers made from the 33/50 aromatics; and

■ paint strippers made from dichloromethane (see Chapter 11) that are used by industry to clean paint from equipment or by consumers to remove old or peeling paint from a substrate.

Many manufacturers are eliminating unnecessary paints and coatings only used for appearance. Others are switching to less polluting, solvent-free or low VOC substitutes. Water-borne paints are gaining popularity in the trade sales sector.

One manufacturer of automobile parts, for example, has found that consumers do not care if certain parts are painted if the paint does not

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provide an engineering function. This manufacturer has eliminated the unnecessary paint and saved money by reducing the amount of materials and equipment used in painting and paint stripping, and material handling and disposal costs. In addition to these and other cost savings, reducing the use of toxic chemicals in the workplace has improved working conditions and resulted in numerous intangible benefits such as improved consumer perception.

Manufacturers who are considering product redesign to eliminate unnecessary coatings must consider the substrate and its characteristics without a coating. If the coating is needed to provide an engineering function, such as improved corrosion resistance, one option may be to change to a base material that does not require a coating. Whether the coating is applied to a substrate to improve its appearance or to provide an engineering function, however, the challenge for manufacturers who want to eliminate unnecessary painting processes can be to convince their clients that painting is not necessary.

Water-Borne Paints and Coatings

Water-borne paints and coatings have the widest potential as safe substitutes for traditional solvent-borne paints, especially in the trade-sales sector. Water-borne paints are categorized as containing water-soluble or water-dispersible binders, depending on the use of water in the product (i.e., as a solvent or diluent).

Water-Soluble Paints. Water-soluble binders are relatively low molecular mass polymers such as alkyds, polyesters, polyacrylates, epoxies, and epoxy esters. The individual molecules of the water-soluble polymers dissolve in water due to salt formation involving functional anionic or cationic groups. Most water-soluble binders are anionic, although cationic electrodeposition paints are also used. Electrodeposition coating is a technology in which negatively or positively charged paint particles are deposited from aqueous solutions onto metallic substrates by application of an electrical field. Primers for metal parts are frequently applied by electrodeposition.

Water-soluble binders are generally produced via polycondensation or polymerization reactions in an organic medium. As a result, they generally contain organic co-solvents like alcohols, glycol ethers, or other oxygen-containing solvents that are soluble or miscible with water (organic content less than 10 to 15 percent). Because of viscosity anomalies, water-borne paints made with water-soluble binders have only about 30 to 40 weight-percent solids content.[24]

Water-soluble binders can be physically, oxidatively, or oven dried; oven drying chemically cures binders with cross-linking agents. Water-soluble paints and coatings may be applied by a number of methods, including dip coating, flow coating, spray coating, and the electrodeposition method described above. Water-soluble coatings tend to be water-sensitive due to the nature of the soluble polymer system. The coatings, however, have a high gloss, high level of corrosion protection, and good pigment wetting and stabilization which are comparable to solvent-based systems.

Water-Dispersible Paints. Water-dispersible paints are the largest product group worldwide in the paint and coating industry.[25] Dispersion paints are also commonly known as latex paints. Latex is a generic term used to describe a stable dispersion of insoluble resin particles in a water system. Use of water-dispersible paints in the U.S. accelerated after World War II because of the decline in postwar demand for styrene-butadiene rubber. Thus, part of styrene-butadiene rubber production capacity was converted to styrene-butadiene latex. Elsewhere, the lack of natural raw materials like vegetable oils for alkyd resins spurred the changeover to synthetic resins.

Most water-dispersible paints dry physically by evaporation of water under ambient conditions. They are also noncombustible in liquid forms, and can be cleaned up with water. Dispersion paints can be used on many types of

substrates in both consumer and industrial applications. Many dispersion coatings that form films and dry at temperatures greater than 40°C are used for the industrial coating of plastic articles and metals.

Resins used in dispersion paints include vinyl acetate co-polymers, vinyl propionate co-polymers, acrylate-methacrylate co-polymers, styrene-acrylate co-polymers, and styrene-butadiene polymers. Dispersion paints contain small amounts of organic solvents (usually less than five weight-percent) as coalescing agents that evaporate on drying.[26]

Vinyl acetate co-polymers and vinyl propionate co-polymers can be formulated to be particularly elastic or weather resistant. Acrylate-methacrylate co-polymers are highly weather resistant and are used for house paints and for water-borne industrial paints. Styrene-acrylate co-polymers are used in interior-use paints, plasters, and some exterior-use paints. The water absorption and elasticity of these polymers decrease with deceasing styrene content. Styrene-butadiene polymers have low water uptake but tend to undergo chalking, and are thus used primarily as interior paints.

Besides water, resin, and pigment, water-borne dispersion paints contain extender auxiliary agents such as dispersants and protective colloids and emulsifiers, thickeners, and preservatives. Preservatives are used to prevent microbial growth in stored emulsion paints. One problem with latex paints had been the addition of mercury to prevent formation of mold and mildew. As the paint dries, mercury vapors were released into the air. This use of mercury was eliminated several years ago from interior latex paints, and recent developments in alternative chemical additives has virtually eliminated this use of mercury in all paints and coatings.

Dispersion paints have relatively high solids content (50 to 60 weight-percent).[27] Because the binder is in particulate form, only a low gloss and, in some cases, only limited corrosion protection can be achieved. This limited corrosion protection is due to the films increased permeability, which makes it difficult for them to

pass salt spray and humidity tests. For example, porous masonry surfaces may experience migration of soluble salts though the film to leave a white deposit on the surface of the coating. On the other hand, the increased permeability of water-borne dispersion coatings allows these coatings to "breathe," or allow moisture vapor to pass through. This decreases the chance for moisture build-up on the substrate which reduces the chance for blistering or peeling. Emulsion paints are less susceptible to blistering and peeling than most solvent paints.[28] Because of their rapid drying properties, water-borne emulsions have only limited use for electrostatic coating and dipping applications. They can be applied by spraying.

Not all properties of solvent-based paints, however, are available with the water-borne alternatives. As discussed above, high gloss and wear resistance are available only from selected paint formulations. Also, water-borne paints and coatings will not remain stable on the shelf as long as solvent-based paints.

No-VOC Water-Dispersible Paints. In 1992, Glidden began to market a no-VOC interior latex paint, Spred 2000, in a limited number of colors. Spred 2000 uses a new technology to form the polymer dispersion, which alleviates many of the problems encountered by other manufacturers who have attempted to use traditional latex technologies and no VOCs. With this new technology, the film formed by the no-VOC paints exhibits characteristics similar to traditional low-VOC latex paints, without the need of a solvent. The paint has tinting capabilities and no odor after application. Glidden is marketing Spred 2000 as a high quality, interior wall paint. After two years on the market, Spred 2000 is doing well in states that have VOC regulations, such as California. Glidden has plans to make all of its paint products without VOCs by the end of the decade. Another paint manufacturer, ICI Subsidiaries, set the year 2000 as the target date to eliminate all VOCs from its decorative architectural coatings.[29]

Applications for Water-Borne Paints. Water-borne paints have quickly taken hold in

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the consumer market, but have been less accepted in market sectors with exceptionally high appearance or engineering requirements, such as the automotive industry. In recent years, however, the automotive OEM sector has increased its use of water-borne paints and coatings in all but the heaviest-coat applications.[30] An estimated 20 percent of this sector now uses water-borne paints, and that percentage is growing each year.[31] With improved water-borne paint technology, manufacturers have been able to change from solvent-borne to water-borne coating systems and meet emissions regulations while maintaining their ultrahigh finish standards.[32]

Traditionally, automobiles are painted using a complicated, four-coat system: an electrocoated primer, a primer-surfacer, a basecoat, and a topcoat/clearcoat. The market for basecoats is moving progressively toward water-borne systems, with powder coatings gaining a stronger market share of the primer, primer-surfacer, and topcoat/clearcoat applications. Du Pont's Generation 4, a water-borne epoxy/polyurethane coating, is currently in use in five automotive assembly plants in North America. PPG Industries is marketing a "full-line" water-borne solution to the traditional solvent-based, four-step system. This switch by the automotive industry, with its extremely high performance standards, is indicative of the quality and performance that can be achieved using water-borne systems. If the automotive industry can change from solvent-borne coatings to water-borne coatings, other industries with similar or less stringent performance requirements should also be able to make the switch.[33]

Hybrid Paints. Hybrid systems consist of combinations of water-soluble and water-dispersible binders. The hybrid systems allow compensation for the disadvantages of water-soluble binders that have low solids and high organic solvent contents and water-dispersible paints that can have problems with film formation. These hybrid binders are now being used as aqueous metallic base paints for automotive coatings and finishes. Hybrid systems generally contain about ten percent organic solvents.[34]

Management of Waste Paint. Many communities have begun collecting latex paints from the household wastestream to reduce the wastes, hazardous or not, entering landfills and incinerators. In 1990, most programs collected latex paints in their original containers or consolidated them in large containers for use without additional processing. The most successful "drop and swap" programs have been able to identify markets for the collected materials.

Paint manufacturers are also developing methods for recycling paints collected from communities and industry. Major Paint, a manufacturer of latex paints, markets three architectural latex paints, Cycle II latex flat, semi-gloss, and primer coatings, made from recycled materials. In the past, manufacturers have had difficulty recycling paint collected from consumers because the paint is frequently contaminated. Major Paint uses a proprietary filtering process and controlled collection practices to sidestep the problems of unknown and cross contamination of the recycled paints. The collected material is mixed with virgin paints and marketed through the federal General Services Administration (GSA) as 50 percent recycled paint (15 percent post-consumer waste). Green Paint Company of Massachusetts has marketed similar recycled products. The GSA in November, 1993 issued draft performance specifications for recycled latex (TTP-28-46) that include a specified minimum post-consumer content, maximum VOC level of 200 g/l, and maximum mercury concentrations.[35]

High-Solids Paints and Coatings

EPA defines high-solids paints as systems with volatile organic contents of less than 2.8 pounds per gallon. High-solids paints are defined elsewhere as paints with more than 85 percent solids content by weight. In practice, paints with a solids content of 60 to 80 percent

may also be called high-solids paints, especially if the equivalent solvent-borne paint contains more than 50 percent solvent.[36]

Oil-based paints and varnishes were the first widely used low-solvent paints, but their use has been largely displaced by the new high-solids paints developed in response to stricter environmental regulations. Today, high-solids paints include low-solvent and solvent-free paints.

To achieve solids contents exceeding 70 percent, the binder in a high-solids paint must be modified to have a much lower intrinsic viscosity than binders of conventional solvent-borne paints. This is usually achieved by developing special binders with reduced number-average or weight-average molecular mass. Nonvolatile reactive diluents, metal compounds, or organic compounds as cross-linking agents are also used. Cross-linking agents assist the reaction of low molecular substances and/or polymers to form macromolecules. Lead and tin compounds have proved particularly suitable as cross-linking agents.[37] The extent of the use of lead and tin for this application was not reported in the literature.

The binders used in high-solids paints include alkyd resins, polyester resins, polyurethanes, acrylic resins, epoxy resins, and poly (vinyl chloride) plastisols. High oil, oxidatively drying alkyd resins are used as maintenance and architectural (trade-sales) coatings. These coatings have a solids content of 85 to 90 weight-percent. Nondrying alkyd resins cross-linked with melamine resins during heat-curing are used for industrial coatings.

Low molecular mass polyesters formulated with melamine resins, isocyanates or polyisocyanates are used in high-solids paints, although high quality paints with a solids content exceeding 70 weight-percent are not widely available. This type of high-solids paints is more widely used for architectural coatings than industrial coatings because of the possibility of postcombustion of the solvent.[38]

Polyurethane-based high-solids paints are being used in both the architectural and industrial sectors. Aliphatic isocyanates with a high

yellowing resistance are seeing increased use. In addition, low-viscosity polyurethane oligomers are combined with polyester, acrylic, and alkyd resins as modifiers for water-borne and low-solvent binders that improve the hardness and the flexibility of the paint film. Epoxy resins are also used with high-solids paints based on acrylic, polyester, or alkyd resins.

Besides the reduction of pollution and the improvement in safety that results from using less solvents, there are several advantages to high-solids paints. High-solids paints save materials, energy costs, and transportation costs. They also provide higher layer thicknesses per application cycle which results in time savings. Perhaps most importantly, high-solids paints can be applied with conventional equipment, which makes them readily accessible to small- and medium-sized facilities and users of trade-sales paints.

High-solids paints must rely on the binder to provide flowability and prevent sagging on vertical surfaces or wrinkle formation. The binder is also responsible for controlling the drying behavior. In a high-solvent paint, these properties are provided, in part, by the solvent. Beyond the possible limitations of providing these properties with a binder, no barriers to the use of high-solids paints were identified in this study.

Powder Coatings

Powder coatings are powdered resins which are applied to a substrate and heated to fuse the resin into a uniform, continuous film. Less than one percent solvent is used in powder coatings and the application process is almost pollution-free.[39] Easy collection and reuse of powdered over-spray is one attribute of powder coating that accounts for its limited waste generation.[40] In addition, the method eliminates the fire and toxicity hazards associated with the use of solvent-based paints and also shows savings in cost.[41]

There are three main methods in use for application of powder coatings: fluidized bed, electrostatic spray, and hot flock. The

electrostatic spray process has a substantially larger market share than in the fluidized bed and hot flocking processes, and is discussed below.

In the electrostatic process, electrostatic forces are used to coat a part with a fine layer of powdered resin. This is accomplished by charging the powdered coating and directing them toward the substrate to be coated. The powdered particles, dispersed and conveyed in an air stream, acquire their charge by passing through a high voltage source. The particles are then attracted and held to the substrate, which is grounded, through electrostatic forces. The substrate is subsequently heated in an oven, or chemically activated (e.g., by infrared), to fuse the particles to the substrate and each other to create a continuous film. The thickness of the powdered layer on the substrate is self-limiting and determined by the combination of powder and source of electrostatic charge.[42]

Coating powders are frequently separated into decorative and functional grades; decorative grades generally have a finer particle size than functional grades. Powders are also divided between thermosetting and thermoplastic resins.[43] Of the thermosetting coating powders, epoxy and polyester-urethane binders had the most production capacity in the U.S. in 1988, accounting for 29 and 32 percent, respectively, of capacity. Polyester-trisglycidyl isocyanurate (21 percent) and epoxy-polyester (17 percent) were next, while acrylic powder coatings only had one percent of the production capacity for thermosetting coating powders.[44] Conversely, epoxy-polyester resins dominate the coating powder market in Europe, where they account for 55 to 60 percent of capacity.[45] The thermoplastic coating resins include polyvinyl chloride, polyamides, cellulose esters, and polyethylene-propylene.[46]

The use of powder coatings in industrial applications produces the least environmental pollution of any of the current coatings technologies. No paint slurry is generated during their application, and dust-air mixtures are easily separated. Powder overspray is easily recovered. Finally, the coating powders are

virtually solvent free and generally cure by polyaddition.

The environmental benefits and the lack of environmental legislation affecting their use or disposal are two reasons why powder coatings are seeing increased use. In addition, powder coatings are economical and are applied using simple, easily-to-automate methods, thus minimizing the training required for operators. Powder coatings also have good film properties, coat corners well, and may be applied in a wide range of thicknesses.

Disadvantages of powder coatings include problems with color changes and limited applicability of the technology. Color matching is more difficult with powder coatings than with solvent coatings. Since powder coatings materials are discrete particles, each of which must be the same color, there can be no tinting or blending by the user. Color must be available from the manufacturer. Finally, the high temperature required to cure the powder coat makes the process applicable only for metals and some plastics that can withstand the temperature extremes.

Powder Coatings in the Automotive Industry. In February, 1993 the Big Three auto manufacturers, GM, Ford, and Chrysler, formed a consortium to explore the expanded use of powder in primer and clearcoat systems. The Powder Coatings Institute anticipates a 12 percent annual growth rate for powder coatings through 1996; another source predicts a lesser growth rate of six to seven percent. Currently, metal finishing, appliances, lawn and garden, and architectural applications of powder coatings represent 53 percent, 21 percent, 8 percent, and 3 percent, respectively, of the total powder coatings market.[47]

Aqueous Powder Suspensions

Aqueous powder suspensions (APS) are powdered resins in slurry form which can be applied with conventional spray guns. They can also be applied by airless spraying, dip coating, electrostatic spraying, and reverse roller coating. APS products do not contain organic solvents and

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can be applied in thinner films than powder coatings.

The APS system is a liquid-solid system which consists of a dispersion of powdered resins, pigments, hardeners, and other additives in water. APS systems do not contain emulsifiers. The typical solids content of an APS paint or coating is from 20 to 30 percent. Thus, they have the disadvantage of requiring more energy for curing than powder coatings or other water-borne systems.

Compared to powder systems, APS systems eliminate the hazard of powder dust. They can also be shaded more easily, and colors switched quickly on the production line. The cost of APS systems is slightly higher than that of powder because their manufacturing process includes an extra wet-grinding step. APS paints and coatings can be used for nearly all types of industrial applications.

Conclusions

In the industrial sector, powder coatings appear to offer the best environmental alternative to solvent-based paints made with the 33/50 chemicals, since these paints completely eliminate the use of the solvent. Water-dispersible paints are the best choice for the trade sales sector since they have the lowest organic solvent content of the water-borne safe substitutes. In addition, paint manufacturers have begun to introduce VOC-free water-dispersible paints, such as Glidden's Spred 2000, no-VOC latex paint. Fortunately, these safe substitutes for solvent-borne paints are rapidly taking hold in industry and the trade sales sector. In fact, water-borne paints held about 80 percent

of the interior coatings market in 1990[48] when powder coatings held eight to nine percent of the total industrial coating market. Currently, powder coatings cannot be used in some sectors of the industrial market, like large outdoor applications such as bridges and ships. When these sectors are excluded, powder coatings held a 15 percent share of the available industrial market in 1990.[49]

The safe substitutes for solvent-borne paints are not without environmental disadvantages, however. Many of the resins used in these paints (methyl methacrylate, polyurethane and styrene-butadiene, to name a few) are made from 33/50 chemicals. Variations of these same resins are also used, however, in high-solvent paints. Whatever the type of paint, therefore, the best environmental solution may be to redesign the product to eliminate unnecessary paints and coatings.

Despite the potential health and environmental issues associated with the resins used in substitutes for solvent-borne paints and coatings, the substitutes represent a big step toward preventing the release of toxic organic solvents by use of safe substitutes. Further research and development should be encouraged to develop substitutes that, for example, meet the appearance requirements of the automotive industry or water-borne paints that have an extended shelf-life. Substantial reductions in the nation's hazardous waste burden and the release of toxic chemicals will be achieved as more industries and consumers switch to the safe substitutes. Industry and consumer interest also provides the impetus for paint manufacturers to increase their research in these areas.

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CHAPTER 9

MATERIALS AND PARTS DEGREASING

Materials and parts degreasing is a process to clean organic materials, water-soluble inorganic salts, and insoluble particles from manufactured materials or parts. Four of the six 33/50 halogenated organic chemicals: dichloromethane (DCM), tetrachloroethylene (PCE), 1,1,1-trichloroethane (TCA) and trichloroethylene (TCE), are used as solvents in industrial degreasing applications. The halogenated organic solvents are used to remove organic materials like rosins, glycols, oils, greases, and waxes from the substrate. Removal of the organic materials will often free the insoluble particles from the substrate.

Concerns about the toxicity of halogenated solvents and the impending phase-out of TCA as an ozone depleting substance have resulted in the recent development of a number of substitutes for solvent degreasing processes. This chapter presents the use of and substitutes for the 33/50 halogenated organic chemicals in degreasing applications.

INDUSTRY PROFILE

Materials and parts degreasing are an integral part of many industrial processes, including the manufacturing of automobiles, electronics, furniture, appliances, jewelry, and plumbing fixtures. Degreasing is also frequently used in the textiles, paper, plastics, and glass manufacturing industries. The five major industry groups that use halogenated solvents in degreasing operations are furnitures and fixtures (SIC 25), fabricated metal products (SIC 34), electric and electronic equipment (SIC 36), transportation equipment (SIC 37), and miscellaneous manufacturing industries (multiple SIC). With the exception of the furniture and fixtures industry, each of these were among the top industries for total TRI releases and transfers of the 33/50 halogenated compounds in 1991 (see Table 3.6).

> *Some of the greatest progress in preventing pollution has been in the area of solvent degreasing processes. Concerns about the potential health and environmental effects of the 33/50 halogenated solvents have helped advance the development of safe substitutes.*

Degreasing is most often employed as a surface-preparation process to remove

contaminants and prepare raw materials and parts for subsequent operations like machining, painting, electroplating, inspection, and packaging. Traditionally, various organic solvents, including DCM, PCE, TCA, TCE, chlorofluorocarbons, petroleum distillates, ketones, and alcohols, have been used either alone or in blends in the degreasing process. Recently, aqueous solvents and other alternatives such as terpenes have seen increased use.

Quantities of 33/50 Halogenated Solvents Used in Degreasing

Based on the chemical-use tree for the 33/50 halogenated organic chemicals (see Figure 3.1) and the 1992 demand data (see Table 3.2), almost 499.9 million pounds of 33/50 halogenated organic chemicals were used as degreasing solvents in 1992. Degreasing is the largest end-use for TCE and TCA, accounting for 90 percent (103.5 million pounds in 1992) of TCE consumption and 49 percent (294 million pounds in 1992) of TCA consumption. DCM and PCE are used as degreasing solvents on a much smaller scale; only 11 percent (42.9 million pounds) of DCM and 13 percent (32.5 million pounds) of PCE (1992).

Price of 33/50 Halogenated Solvents Used in Degreasing

The current prices of the 33/50 halogenated organic chemicals used as degreasing solvents range from $0.29 for bulk quantities of PCE up to $0.64 per pound for bulk quantities of TCA (see Table 3.3). Other costs associated with degreasing include solvent recycling or recovery costs (or solvent replacement costs if the solvent is not recyclable), energy costs, and waste disposal costs.

One cost advantage of the 33/50 halogenated compounds as degreasing solvents is that they are relatively easy to recycle and recover using distillation equipment. Waste materials generated from the degreasing process or from a solvent recovery system, however, must be disposed of as a hazardous waste.

DESIRED PROPERTIES OF DEGREASING SOLVENTS

A good degreasing solvent should have excellent solvency for a broad range of organic materials, particularly oils and grease. The solvent should preferably be nonflammable, especially in vapor degreasing applications (described below), and be noncorrosive to the metals or parts being cleaned and the degreasing equipment. A good degreasing solvent should also have low toxicity. Additional properties desired in a degreasing solvent include a low heat of vaporization, a high vapor pressure that allows evaporative drying of cleaned parts, and chemical stability.

The 33/50 halogenated solvents have been extensively used in the industrial applications cleaning, primarily because of their excellent solvency, nonflammability, and high vapor pressures. Additionally, their vapors are heavier than air and thus can be contained somewhat within the degreasing equipment. Only recently have health, safety, and environmental issues concerning their use and disposal contributed to a decrease in their use as degreasing solvents and to a search for substitutes.

DEGREASING PROCESS DESCRIPTION

The three basic types of degreasing equipment are cold cleaners, open-top vapor degreasers, and conveyorized degreasers.[1] The processes for metal or parts degreasing with these types of equipment are discussed below.

Cold Cleaning

Cold cleaners are usually the simplest and least expensive of the three types of degreasing equipment. Parts are cleaned by being immersed and soaked, sprayed, or wiped with solvent. A typical cold cleaner consists of a tank filled with solvent and a cover for periods of nonuse. More sophisticated cold cleaners are equipped with solvent sumps, spray nozzles, drains, and automatic controls.

In the basic cold cleaning process, soiled objects are dipped into the solvent bath to dissolve the contaminants from their surface. This cleaning process can be enhanced by agitating the solvent, or by brushing or spraying the solvent onto the soiled objects. Cold cleaning is usually conducted at room temperature and ambient pressure, although in some cases the solvent may be heated, but not above its boiling point. When the parts are removed from the immersion bath, solvents are allowed to drain and evaporate from the parts.

Vapor Degreasing

The vapor degreasing process uses the vapor of the cleaning solvent to remove contaminants from materials or parts. The vapors, generated by boiling the solvent, condense on the relatively cold parts, dissolving and displacing the contaminants and soils, thus cleaning the surface. Cleaning ceases when the parts and vapor temperatures are at equilibrium.

The open-top vapor degreaser is a large tank with three distinct zones: the solvent reservoir, vapor zone, and freeboard. The solvent reservoir, which contains the cleaning solvent, is equipped with electric or steam heater coils to create the vapor zone by boiling the solvent. The vapor zone, directly above the solvent reservoir, is the zone into which the relatively cold parts are lowered causing vapor condensation and thus parts cleaning. The vapor zone height is controlled by cooling coils located near the top and on the inside perimeter of the tank. The coils condense the solvent vapors and return them as liquid to the reservoir. The density of the solvent vapors, as previously mentioned, also assists in maintaining a vapor zone and containing the vapors within the tank. The freeboard is the vacant space above the vapor zone which minimizes solvent drag-out when the parts are removed from the vapor zone after cleaning. The freeboard space allows condensed solvent vapors to drip from the cleaned parts, as well as offering drying time for the parts. Much of the solvent vapors and liquid

in this zone fall back to the vapor zone and reservoir.

Vapor degreasing is frequently more advantageous than cold cleaning because the cold solvent bath becomes increasingly more contaminated during the cleaning process. As the cold bath becomes more and more contaminated, the relative cleanliness of the parts may decrease because the parts are in direct contact with the contaminated liquid solvent. In vapor degreasing, although the boiling liquid solvent in the reservoir contains the contaminants from previously cleaned parts, contaminants usually boil at higher temperatures than the solvent, resulting in the formation of essentially pure solvent vapors. In addition, the high temperature of vapor cleaning aids in wax and heavy grease removal and significantly reduces the time it takes for cleaned parts to dry.

Conveyorized Degreasing

Conveyorized, or in-line, degreasers have automated, enclosed conveying systems for continuous cleaning of parts. Conveyorized degreasers clean by either the cold solvent process or the vaporized solvent process. While these units tend to be the largest degreasers, they actually produce less emissions per part cleaned than other types of degreasers. This is due primarily to the enclosed design of the conveyor systems.

Hybrid Degreasing Systems

Combinations of immersion and vapor degreasing systems can be employed to aid in the cleaning of problematic soils (e.g., waxes), or highly soiled parts. These hybrid units can utilize agitated solvent baths, spray units and/or ultrasonics in conjunction with vapor degreasing processes. Ultrasonics applies energy to a cleaning solution to induce cavitation, or the collapse of millions of tiny bubbles produced in the solution by the applied energy. It is the collapse of these bubbles that create a scrubbing effect to clean the immersed parts.[2]

ENVIRONMENTAL RELEASES FROM DEGREASING

Environmental releases from the use of 33/50 halogenated compounds in degreasing occur from their production through the degreasing process and the final disposal of solvent residuals, as discussed in the following sections.

Releases and Transfers from Production and Distribution Facilities

Releases from the production of 33/50 halogenated organic were obtained from the 1991 TRI data and discussed in Chapter 3. Total environmental releases and off-site transfers of DCM, PCE, TCA, and TCE from production facilities were more than two million pounds. Since approximately 37 percent of these chemicals produced in the U.S. are consumed in degreasing applications, some fraction of these releases can be associated with halogenated solvent degreasing. Similarly, some of the halogenated organic emissions from distribution facilities are associated with their distribution to degreasing facilities.

Almost all of the DCM and TCE sold and approximately 70 to 75 percent of the PCE sold are distributed through distribution facilities. Distribution facilities are not required to report their emissions in TRI, but in 1983 EPA estimated that approximately 1.28 million pounds of DCM, PCE, and TCE combined were emitted from these facilities.[3] DCM contributed almost 85 percent of these emissions, but DCM only represents about eight percent of the halogenated organic compounds used in metals and parts degreasing. No information was available on the amount of TCA distributed through these facilities or the amount of TCA emissions from distribution facilities.

Releases and Transfers from the Degreasing Process

Environmental releases from the degreasing process include evaporation losses from solvent baths, solvent carry-out, and equipment leaks. Air, water, or land releases occur from solvent recycle and recovery processes, storage and handling, accidental spills and leaks, and disposal of solvent-contaminated residuals as hazardous waste. Because of the wide-spread use of the halogenated solvents in various industry groups, no attempt was made to retrieve the releases and transfers that could be attributed to degreasing operations from the 1991 TRI. However, the magnitude of the environmental releases is illustrated by estimating air releases from the degreasing process.

The range of EPA emission factors for degreasing with DCM, PCE, or TCE is 0.57 to 0.92 pounds emitted per pound of fresh (virgin) solvent used.[4] The lowest emission factor is for open-top vapor degreasers equipped with control devices, such as a cover for the tank, a raised freeboard equipped with a freeboard chiller, and a carbon adsorber. The highest emission factor is for a vapor degreaser without control devices. Applying these emission factors to the almost 500 million pounds of 33/50 halogenated organic chemicals that were estimated used in degreasing operations in 1991 indicates that somewhere between 285 and 460 million pounds were emitted to air. This does not include losses to water or land or disposal of hazardous waste contaminated with the 33/50 halogenated organic chemicals, but 90 percent of total releases of these compounds reported in the 1991 TRI were to air. The lower emission estimate of 285 million pounds correlates well with the total reported releases and transfers of DCM, TCE, TCA, and PCE, approximately 300 million pounds in 1991.

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

As discussed in Chapter 3, all of the 33/50 halogenated organic chemicals are toxic, and DCM, PCE, and TCE are suspected carcinogens. In addition, TCA is being phased-out of production as an ozone-depleting substance, while TCE and PCE are precursors to photochemical smog formation. Today, concerns about the toxicity of the 33/50 halogenated solvents and their potential to

contribute to photochemical smog or ozone depletion have resulted in a reduction in their use in degreasing applications.

Still, market sources have indicated that TCE is being evaluated as a possible substitute degreasing solvent for TCA, since TCA is being phased-out of production as an ozone-depleting substance.[5] Ironically, TCA first gained wide acceptance as a degreasing solvent as a less toxic substitute for TCE, following wide-spread concern about the toxicity of and potential for worker exposure to TCE.

EVALUATION OF SAFE SUBSTITUTES FOR THE 33/50 DEGREASING SOLVENTS

Safe substitutes approaches to reducing the use of 33/50 halogenated organic chemicals in the degreasing process include:

■ using no-clean manufacturing methods;

■ substituting safe, aqueous, or semi-aqueous degreasing solvents for the 33/50 halogenated organic solvents;

■ substituting safe, non-aqueous degreasing solvents for the 33/50 halogenated organic solvents; and

■ substituting non-liquid cleaning technologies for the degreasing process.

Many of these approaches are already seeing wide-spread use because of pending or potential regulations affecting the 33/50 halogenated solvents and their potential to contribute to photochemical smog or ozone depletion. The following sections present evaluations of the substitutes.

No-Clean Technologies

The most fundamental technique for eliminating the use of degreasing solvents is to design processes and/or use materials that do not require cleaning. This is most readily achieved when designing new products or new manufacturing processes. Still, existing facilities may realize cost savings and dramatically decreased potential liability by reconsidering their existing processes and developing alternative methods that do not require cleaning.

Reconsidering an existing process means evaluating the present cleaning operation, as well as the process line, both up-stream and down-stream of the cleaning step. Up-stream of the cleaning step, processes that introduce the soils (oils, greases, etc.) that must later be removed should be evaluated to determine whether alternative materials can be substituted that do not require cleaning, or whether the soil material can be eliminated completely. An example of a no-clean technology is the replacement of lubricating oils with a mineral spirit-based "evaporative oil." Due to its relatively high vapor pressure, the mineral spirit-based oil can be removed using flash-drying or other technologies such that the substitute does not require cleaning prior to subsequent operations.

Considering process requirements down-stream, the current degree of cleanliness specified may not be required to satisfactorily perform the next manufacturing step. In some cases, cleaning may not be required at all. Further, the manufacturing processes can sometimes be rearranged to require fewer cleaning steps.

Developing alternative methods that do not require cleaning means reevaluating the steps in the manufacturing process which introduce materials that must be cleaned. For example, the printed circuit board industry has developed no-clean flux technologies that eliminate the need to clean flux from some printed circuit boards. Unfortunately, use of new technologies is often stymied by their lack of working history. In 1992, no-clean flux technologies had not been introduced into the U.S. Department of Energy (DOE) Weapons Complex because of concerns about the long-term reliability of the printed circuit boards.[6] Similarly, other industries that are required to comply with government specifications may have difficulty introducing no-clean technologies that require process modifications or product redesign.

Specifications for manufacturing parts for the military often dictate the type of cleaning solvent and the cleaning process to be used. Unfortunately, changing government specifications is a long and arduous process that may slow progress in the use of safe substitutes.

No-clean processes require innovative, optimized manufacturing to eliminate cleaning. They save time and chemicals and reduce the regulatory burden and potential liability that results from using hazardous chemicals. The disadvantages of no-clean technologies are that they may require process modifications and even product redesign.

> *The most fundamental technique for eliminating the use of degreasing solvents is to redesign the production process to eliminate the need for cleaning. Other technologies, such as aqueous cleaning systems, are also viable substitutes.*

Aqueous and Semi-Aqueous Solvent Substitutes

In the metal parts and metal finishing industries, aqueous and semi-aqueous cleaners are potential substitutes for solvent vapor degreasers. Some printed circuit board and electronic manufacturers have changed to these systems, however, this industrial sector has been reluctant to change due to the high degree of cleanliness needed and lack of documented successes. Aqueous cleaning solutions include alkaline solutions, detergents, and hot-water washes. They are often used with pressure, agitation, ultrasonics, filtration, or some other physical process to provide effective cleaning in many industrial cleaning applications. Semi-aqueous cleaners are emulsions of hydrocarbon solvents and water. They can also be used with pressure, agitation, ultrasonics, or other physical processes to enhance their cleaning characteristics. The toxicity and effects of chronic exposure to many of the semi-aqueous cleaners have not been fully evaluated. Significant changes in the characteristics of

wastewater and wastewater flowrate are also issues that must be considered when changing to aqueous and semi-aqueous cleaning systems, and are addressed below.[7]

Aqueous and semi-aqueous cleaners are not usually drop-in replacements for halogenated cleaning solvents. These cleaning alternatives usually require the addition of rinsing and drying steps after cleaning to accomplish comparable solvent degreasing results. Water-based cleaners have little or no volatile components, which means that cleaning cannot take place in the vapor phase. Therefore, immersion tanks are most commonly used for these applications in conjunction with heat and agitation. Agitation can be accomplished with ultrasonics or by mechanically rotating the parts and/or circulating the solution. Vapor degreasers and other solvent cleaning processes can be modified to accommodate water-based cleaners. Large vapor degreasing units can be converted to multiple tanks, and modified to incorporate spray rinsing, immersion, ultrasonics, mechanical agitation, filtration, or other methods.[8] Immersion tanks that have a means for adequate skimming of floating oils could be the most useful aqueous/semi-aqueous method of cleaning blind holes and complex geometries.

Aqueous Cleaning. Aqueous cleaning, or parts washing, has been used for years to remove salts, rust, scale, and other inorganic soils from ferrous metals. As a potential substitute for solvent vapor degreasing and CFC cleaning, aqueous cleaning systems may require additives to enhance their soil removal capabilities.[9] Cleaned parts may also require rinsing to remove residual cleaners and drying to prevent corrosion. Some cleaning solutions also require treatment before disposal.

Some additives of aqueous cleaning systems include synthetic detergents and organic surfactants, saponifiers, acids and alkalies, and corrosion inhibitors. The combination of additives selected alter the foaming, wetting, and soil removal properties of the solution.[10] Detergents and surfactants are surface-active agents that emulsify insoluble solids into the solution. Saponifiers change water-insoluble fats

and fatty acids into water-soluble soaps. Oxidants may be added to loosen rust and stains for easy removal. Other additives are used to penetrate the soils and wet the surface of the materials to be cleaned, to precipitate or float the soils, and to neutralize the material. Depending on the requirements of subsequent operations, rinsing may be required to remove residual films left by these additives in the cleaning process.[11] Large suppliers will typically formulate cleaners designed for the particular soils to be cleaned and the subsequent production process.

Aqueous cleaners must be carefully evaluated for their compatibility with the materials being cleaned and the cleaning equipment. Acid and alkaline cleaners may attack some metal substrates. Caustics or strong alkalies will aggressively attack aluminum and zinc. Strong acids will attack steel. Strong oxidizing acids like nitric acid and chromic acid will attack copper. The application of ultrasonics in an aqueous system can also increase the corrosiveness of the solution.[12] In addition, alkaline cleaning systems sometimes have problems with surface oil recontamination of the parts, rapid fluid depletion, long cleaning time, and high maintenance.

Success has been observed by companies with spray systems utilizing hot water solely as the cleaning medium. Cutting oils, cooling fluids, and other soils can be effectively removed by a hot water spray. Many of the compatibility problems with aqueous additives mentioned above can be avoided by the use of a hot water system, and wastewater treatment issues may be simplified. Ease of operation can also be an added benefit of a hot water spray system; the oils and greases separate more quickly from the water phase (float to the water surface) than would be observed with detergents or surfactants. This allows for skimming of the oils and grease and easy water recirculation. Eliminating the need for monitoring and adjusting the concentration of additives in the aqueous solution can also free operator time for other activities.

The treatment and disposal of the aqueous cleaning solutions is an important consideration when changing to an aqueous system. The use of additives in the aqueous solutions cause many of the disadvantages of these cleaning systems. Some additives create new health and safety or treatment and disposal issues. Detergents and surfactants may not be readily biodegradable; the solutions pH may be unacceptable for direct discharge; cleaning solutions containing saponifiers tend to have high biological oxygen demands (BODs) which may exceed limits in National Pollutant Discharge Elimination System and POTW pretreatment permits. As a result, pretreatment prior to discharge to the sewer system may be required to meet local, state, or federal requirements. As a response to these disposal issues, "closed-loop" aqueous cleaning systems have been developed which minimize the process water that must be treated and concentrate the oils and other contaminants for disposal. These closed-loop systems can include filtration (micro or ultra), gravity separation, adsorption, and chemical treatment units which recirculate the water back to the cleaning system and concentrate the contaminants.[13]

Semi-Aqueous Cleaning. Semi-aqueous cleaning processes use organic solvents, usually in combinations with a surfactant, and in combination with water. The semi-aqueous solvents include terpenes, dibasic esters, glycol ethers, and n-methyl pyrrolidone (NMP). In semi-aqueous cleaning these solvents are utilized in one of the following three applications: 1) as emulsions in water; 2) in concentrated form, followed by water rinsing; or 3) a combination of these two applications.

Because these chemicals represent another group of organic solvents, issues similar to those associated with chlorinated vapor degreasing solvents must be considered. The excellent solvency of these chemicals allows for the effective removal of difficult soils such as heavy oils, greases, tars, and waxes. The flammability and photochemical reactivity must be considered when designing the process (i.e., limited

applications using heat and atomized spraying units). The low volatility of these chemicals minimizes the potential for worker exposure but also results in slow drying of the parts. A final water rinse may be required to remove chemical residuals.

Terpenes are citrus or pine-based biodegradable hydrocarbon solvents extracted from citrus peels or pine trees. Glycol ethers are synthetic organic chemicals mainly produced by the reactions of epoxides (ethylene oxide or propylene oxide) with alcohols. Dibasic esters and NMP are discussed in more detail in Chapter 11. Petroleum-based hydrocarbons, also frequently used in semi-aqueous applications, are not recommended in this report if they contain 33/50 aromatics. Some additives may also create new health, safety, treatment, and disposal issues. For example, some glycol ethers are toxic. The toxicity of many terpenes is not well defined. In additions, terpenes are not as easily recycled because they chemically bond to the soils they remove. However, most of the solvents are readily incorporated into a closed-loop recycling system; the water can often be recovered for re-use, and the cleaner must be disposed of, possibly as a hazardous waste. In the electronics industry, terpenes have been found to be an effective substitute for CFCs in the removal of flux from printed circuit boards.[14]

As with aqueous cleaning systems, the treatment and disposal of semi-aqueous wastestreams, both chemical and water, must be addressed when considering this alternative to vapor degreasing. Pretreatment operations similar to those employed in aqueous cleaning still apply to these systems: filtration, adsorption, gravity separators, and chemical treatment. One problem may be encountered when trying to separate the solvents from the water in a timely fashion. This can result in a contaminated recirculated water stream, significant organic discharges, and a solvent wastestream which is not easily recoverable. Proper design of decanting tanks, adequate allotment of process time, and the use of "second-generation" solvent blends which

separate more quickly from the water can alleviate this problem. The solvent wastestream can either be disposed of, or treated by vacuum distillation to recover the pure components. Fuel blending of the solvent wastestream, recovering the solvents' BTU values, is also a possibility.

Non-Aqueous Solvent Substitutes

Non-aqueous substitutes include hydrocarbon blends, alcohols, ketones, and HCFCs. Non-aqueous substitutes are limited drop-in substitutes for existing cleaners. They often have health, safety, and disposal issues associated with their production, use, and disposal that are similar to those of the halogenated solvents. Many of the non-aqueous substitutes are regulated and some may be phased out in the future.

Alcohols, ketones, and hydrocarbon solvents are presently used in some industrial sectors (e.g., manufacturing and repair) for cold cleaning applications. The hydrocarbon solvents are usually combined with a surfactant and rust inhibitor. Hydrocarbon blends, alcohols, and ketones are effective in removing soils such as cutting oils, coolants, greases, and waxes. These compounds can also be effectively recycled. Disposal options generally involve incineration. Several characteristics of these cleaners, however, limit their drop-in applicability. All have low flash points which restrict their use in enclosed systems and vapor degreasers. Spraying is also not an option because the small droplets can ignite below the flash point of the bulk fluid. Finally, these alternative cleaning solvents exhibit slower drying times than traditional solvents, thus requiring an added drying step, and/or increased processing time.[15]

For other applications, such as replacing DCM in special cleaning applications like wiping or paint gun cleaning, combinations of NMP and dibasic esters (DBE) are being used. NMP and DBE are discussed in more detail in Chapter 11 which presents their use as substitute paint strippers.

Three HCFCs developed to replace CFCs as a cleaning agent, HCFC-141b, HCFC-123, and HCFC-225, have had limited exposure to the

commercial market. The solvency powers of these HCFCs are between those of CFC-113 and 1,1,1-trichloroethane, and their boiling points are lower, thus having the potential to be drop-in alternatives in the existing CFC equipment. However, based on the results of toxicity testing, the existing worker exposure standard for 123 has been lowered, and tests involving the isomers of 225 may show some toxicity.[16] All three compounds have already come under phase-out legislation by the year 2015 (except in refrigerant applications).

Non-Liquid Technologies

Non-liquid technologies include media blasting and supercritical carbon dioxide (CO_2) cleaning. Because these technologies clean parts without using liquids, they produce less waste. Until recently, however, blasting and supercritical technologies have been limited to sturdy parts. Equipment costs are relatively expensive.

When the temperature and pressure of a substance such as CO_2 are raised above the critical point, the result is a supercritical fluid with unique properties. For CO_2 the critical point is at 31°C and 72.9 atm. Supercritical fluids possess high diffusivity, low density and viscosity, and powerful solvency properties, all of which contribute to the fluid's effective cleaning capabilities. By controlling the pressure and temperature of the supercritical fluid (thus controlling the solvency properties), contaminants can be dissolved and cleaned from the substrate. This technique is particularly appropriate for the cleaning of intricate precision parts, if they can withstand the extreme temperatures and/or pressures. Supercritical fluids, however, do not appear effective for removing ionic contaminants and particulate materials.

Media blasting uses the abrasive and/or fractioning action of a propelled media to remove the contaminants from the soiled part. The technique of media blasting has been used for years to remove corrosion products, heat scale, and carbon deposits on metal parts. Two

examples of media blasting materials are solid CO^2 crystals or pellets and sodium bicarbonate. The recent development of small, supercritical CO_2 crystals, called CO_2 "snow," makes CO_2 media blasting effective in removing light organics and particulates from more precise and delicate metal surfaces. Carbon dioxide snow blasting minimizes the potential for damage to the part's surface, and minimizes the amount of waste generated. Upon contact with the surface and removal of the soils, the CO_2 instantly sublimes. Carbon dioxide blasting is not effective for cleaning oil and grease, however, and cannot effectively clean parts with crevices or blind holes.[17]

Sodium bicarbonate media blasting is an alternative media blasting technique which could potentially remove oils and greases. This technique uses an aqueous slurry of water and sodium bicarbonate under high pressure to remove soils. Tests are currently underway to determine the applicability of this technology beyond its current industrial applications.

Conclusions

Substantial progress has been made in the use of safe substitutes for the toxic, 33/50 halogenated organic cleaning solvents. Examples of industries that are switching to safe substitutes range from the printed circuit board industry, to the automotive parts industry, and portions of DOE's Weapons Complex.[18]

Aqueous and semi-aqueous cleaners have the broadest range of application as safe substitutes for the 33/50 halogenated cleaning solvents. Still, a number of disadvantages exist to using aqueous and semi-aqueous cleaners in place of halogenated solvents. In particular, some of the solvent alternatives may be flammable, corrosive, or have limited or no toxicity data. In addition, switching to aqueous or semi-aqueous cleaners and processes generally requires additional equipment, multiple cleaning and rinsing steps, and drying, depending on the cleaning level currently being attained in vapor degreasers and other solvent-based cleaning processes. Substitutes typically require process

and facility testing in order to determine optimum cleaning chemistries and equipment. Thus, more than one cleaning system may be required to replace one solvent vapor degreaser.

One possible alternative to avoid these problems associated with aqueous and semi-aqueous cleaners is a no-clean technology.

Eliminating the cleaning process significantly decreases the use of any potentially toxic chemicals. Redefining cleanliness specifications, eliminating a step which soils the part, or changing the nature of the soil to eliminate the need for cleaning are only some of the potential ways to implement this alternative.

ENDNOTES

[1] *Survey of Trichloroethylene Emission Sources*, US EPA, Pub. No. EPA-450/3-85-021, (Research Triangle Park, NC, July 1985).
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[9] Ibid.

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[11] "Solvent Cleaning (Degreasing)," Center for Emissions Control, November 1992.

[12] Ibid.

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[14] Liz Harriman, "The Search for Safe, Effective Solvent Substitutes," *Professional Engineering TURA Report*, Vol. 2, No. 2, Spring 1992.

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[16] Ibid.

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[18] Ann C. Finklin and Gordon L. Hickle, "Materials Substitution at the Rocky Flats Plant," *The Environmental Challenge of the 1990s*, (Washington: Environmental Protection Agency, Pollution Prevention Office, 1990).

CHAPTER 10

DRY CLEANING

Dry cleaning is a process that uses a nonaqueous organic solvent for removing soils, stains, and oils from textile products, fabrics, and garments. It is used primarily for cleaning natural fibers and materials, such as silk, cotton, wool, and leather, that experience shrinkage or water damage from aqueous cleaning. Some synthetic fabrics, such as rayon derived from cellulose, are also dry cleaned.

This chapter describes the use of and substitutes for the 33/50 halogenated organic chemical tetrachloroethylene (PCE) as a dry cleaning solvent. Both PCE and 1,1,1-trichloroethane (TCA, another 33/50 halogenated organic chemical) are used in dry cleaning, but TCA has only a small market share in this application. TCA use is also declining because of its planned phase-out as an ozone depleting substance.

> *Dry cleaning is the single largest use of PCE, one of the 33/50 halogenated organic compounds. In recent years, providers of professional garment care have begun to reassess the traditional dry cleaning process to identify safe, effective alternatives to PCE-based processes.*

INDUSTRY DESCRIPTION

The dry cleaning industry consists of an industrial sector, a commercial sector, and coin operated dry cleaners. In 1991, there were an estimated 25,200 existing commercial and industrial dry cleaning facilities throughout the U.S., compared to approximately 1,600 coin operated facilities.[1] More recent estimates place the number of commercial dry cleaning shops in the U.S. at more than 34,000.[2]

Industrial dry cleaners are large dry cleaning plants that typically rent uniforms, linens, or similar items to businesses, industries, and institutions. Industrial laundry facilities use both dry cleaning and water-based cleaning equipment. EPA projects that the use of dry cleaning in industrial laundry facilities will decline during the five year period from 1991 to 1996 because many of these facilities are switching from the use of solvents to the use of water and detergent.[3]

Industrial dry cleaners typically use transfer machines where clothes are washed in one unit and then transferred to a separate unit to be dried. A typical industrial dry cleaning plant has one dry cleaning system consisting of a 750 pound-per-load capacity washer/extractor and three to six 80-pound-capacity dryers.

Throughput for a typical facility averages approximately one million pounds per year.[4]

Commercial dry cleaners are usually small neighborhood dry cleaning facilities, which are either independently owned or franchise shops. PCE is used by almost 75 percent of the commercial dry cleaning sector. Petroleum blends are used by most of the remaining commercial dry cleaners,[5] with only about 50 dry cleaning facilities known to use TCA.[6] Commercial facilities employ either transfer machines or dry-to-dry units, which wash and dry the clothes in a single unit. The capacity of transfer machines in the commercial sector usually ranges from 35 to 100 pounds per load. A typical commercial facility that uses transfer machines has one dry cleaning system that consists of a washer/extractor and dryer, with an annual throughput of about 39,000 pounds.[7] The current available market of new dry cleaning machines is comprised almost exclusively of dry-to-dry machines with built-in refrigeration controls.[8]

Coin operated cleaners are usually part of neighborhood laundromats, which offer dry cleaning on an over-the-counter basis or a self-service basis. They provide low cost dry cleaning but not pressing, spotting, or associated services. PCE is used by almost 98 percent of these facilities; petroleum cleaning solvents are not used at coin operated facilities.[9] Coin operated dry cleaning shops use dry-to-dry units. Machine capacities range from 8 to 25 pounds per load. A typical installation has two or three machines and an annual throughput of roughly 20,000 pounds.[10] Currently, there is a negative growth rate for coin operated facilities because existing facilities are not being replaced.[11]

Quantity of PCE Used in Dry Cleaning

As shown on the chemical-use tree diagram for the halogenated organic compounds (Figure 3.1), an estimated 50 percent of the PCE used in the U.S. is used by the dry cleaning industry.[12] At the 1991 demand rate, this equates to 125 million pounds per year. EPA estimated, however, that existing dry cleaning facilities emitted 185 million pounds of PCE in 1991.

This estimate suggests that dry cleaning accounts for a larger proportion of the PCE used in 1991, or that the demand for PCE in 1991 was higher than estimated.

Price of PCE Used in Dry Cleaning

Solvent economics play an important part in dry cleaning. The total cost of supplying a retail plant, which includes solvent, other chemicals, hangers and packaging materials, ranges from 9 to 11.5 percent of all costs.[13] The price in January of 1994 for the dry cleaning grade of PCE was $0.28 per pound (tanks and delivered), compared to $0.29 per pound for industrial grade PCE.[14]

DESIRED PROPERTIES OF DRY CLEANING SOLVENTS

Factors that are considered when selecting a dry cleaning solvent include processing features, garment compatibility, and safety and health related issues. A dry cleaning solvent should have a high affinity for greases and oils and a low affinity for fabric dyes. The solvent must not corrode the common metals used in dry cleaning equipment, and be chemically and thermally stable under the variety of conditions experienced in the dry cleaning process. The solvent should also be compatible with the detergents and spotting chemicals used as supplements. The solvent should be sufficiently volatile to leave the garment free of odors after drying and evaporate at a sufficiently low temperature to protect the fabric from damage in the drying process. A low boiling point is also preferred to allow separation of the solvent from contaminants and detergents during solvent recovery by distillation.

A dry cleaning solvent should also be safe in terms of human health and toxicity. Worker exposure may occur from storage and handling of the solvent, from process emissions, and from fugitive emissions. Although PCE is nonflammable, OSHA and some state and local governments have moved to place controls on PCE emissions from dry cleaning facilities

because of concerns about its toxicity. In addition, EPA recently issued rules that regulate PCE emissions from dry cleaning facilities as a hazardous air pollutant (HAP) under the Clean Air Act Amendments of 1990. Nevertheless, PCE dominates the world market for dry cleaning solvents because it is the most successful, nonflammable replacement for petroleum blends.

DRY CLEANING PROCESS DESCRIPTION

The basic dry cleaning process is similar to ordinary laundering processes, except that an organic solvent is used in place of water. The principal steps of the process are one or more solvent-wash cycles, physical extraction of the excess solvent using a spin cycle, and tumble drying. The same steps are employed for both transfer and dry-to-dry machines.

Prior to the solvent-wash cycle, professional garment cleaners inspect garments for stains and heavily soiled areas. These areas are spot cleaned using additional chemicals, steam, and scrubbing; TCA is a commonly used pre-spotting chemical. Next, garments are sorted by color or fabric, and evaluated to choose which washing method to use, either laundering (aqueous washing), dry cleaning (solvent washing), or hand washing. After drying, garments are finished by steaming, then pressing. Steaming is also used to remove water soluble materials remaining after the wash cycle and to kill bacteria.

The action of the solvent on the garment fibers removes solvent-soluble oils and greases and the mechanical tumbling action removes insoluble soils. Lower surface tension enables the solvent to penetrate the fabric, which in turn allows insoluble soils to be more easily removed by the mechanical tumbling action. The solvent is continuously filtered during the washing cycle to remove the insoluble soils.

During the extraction step, most of the solvent is removed from the garments, which are then tumbled with heated air. The temperature of the

air and the length of the drying cycle are determined by the solvent used and by the garments' fabric and construction.

To partially recover and reuse the solvent, the treatment of dry cleaning solvent by filtration, distillation, and charging is performed at some dry cleaning facilities. Filtration removes the insoluble solids, called muck, from the used solvents. Filters may also contain activated carbon that removes dye residues. Solids are removed from the filters daily, and solvent contained in the muck is usually recovered by distillation.

Distillation is used to remove the soluble, nonvolatile residue which accumulates in the solvent. Following distillation, the solvent is "charged" by adding a small amount of water and detergent to the solvent. The detergent, usually added at concentrations of 0.50 to 1.25 percent by volume,[15] helps remove water-soluble stains and enables the system to carry moisture above the solvent's usual water-saturation point. Most of the dry cleaning detergents used are anionic.

ENVIRONMENTAL RELEASES OF PCE FROM DRY CLEANING

Environmental releases from the use of PCE in the dry cleaning process occur from the production of PCE through the dry cleaning process and the final disposal of PCE residuals. The following presents the environmental releases from production and distribution of PCE followed by the releases from the actual dry cleaning process.

Environmental Releases from Production and Distribution

Emissions from PCE production facilities were obtained from the 1991 TRI data and discussed in Chapter 3. Total environmental releases and off-site transfers of PCE from production facilities in 1991 were almost 800,000 pounds. Using a life cycle approach, approximately 50 percent of these releases can

be associated with the dry cleaning industry, since 50 percent of the PCE produced in the U.S. is consumed in dry cleaning.

Approximately 70 to 75 percent of the total PCE produced is distributed through distribution facilities; the remaining 25 to 30 percent is generally sold directly to CFC producers.[16] Distribution facilities are not required to report their emissions in TRI, but in 1983 it was estimated that 110,000 pounds of PCE were emitted to the atmosphere from these facilities.[17] Again, using a life cycle approach, approximately 50 percent of the PCE emissions from distribution facilities can be associated with PCE distributed to dry cleaning facilities.

Specialty chemical plants sometimes prepare product formulations containing PCE for use in dry cleaning. These facilities are classified under SIC 2842, and are required to report emissions to TRI. The 1991 emissions of PCE from these specialty chemical plants reported in the TRI are shown in Table 10.1.

In 1991, more than 20,000 pounds of PCE were reported released from the specialty chemical producers, primarily to air. These release figures may also include emissions from facilities that prepare other types of specialty cleaning, polishing, and sanitation formulations that use PCE, and are not used for dry cleaning.

Environmental Releases from Dry Cleaning Facilities

Air emissions of PCE from dry cleaning plants occur from equipment vents, from chemical and clothing transfer and handling, and from leaks in the process equipment. Emissions also occur from waste materials such as the dryer and filter muck and spent filters from carbon absorbers.

The most significant point of process-type PCE emissions is the dryer vent, where residual PCE or vapors are exhausted from the dryer or dry-to-dry unit. PCE is also emitted from the washer vent in transfer machines. Process-type emissions are also associated with the auxiliary equipment that is used to filter and distill the dirty solvent. These emission points include vented emissions from muck cookers, oil cookers, and other distillation equipment.

TABLE 10.1. RELEASES AND TRANSFERS OF PCE FROM SPECIALTY CLEANING, POLISHES AND SANITATION GOODS PRODUCERS (SIC 2842)

Medium	Release or Transfer (lbs/yr)
Air Release	16,059
Water Release	0
Land Release	1
Underground Injection Release	0
TOTAL ON-SITE RELEASES	16,060
POTW Transfer	260
Other Off-Site Transfer	3,766
TOTAL OFF-SITE TRANSFERS	4,026

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

Fugitive emissions account for approximately 50 percent of the PCE emissions from a dry cleaning facility.[18] These emission sources include the following:

- evaporation that occurs during the transfer and handling of clothing;

- leaks from pumps, valves, flanges, and seals;

- losses during solvent loading and unloading; and

- evaporation of PCE from stored solid waste, which includes spent filters and distillation residue.

EPA recently published a final rule for the National Emission Standard for Hazardous Air Pollutant (NESHAP) that will regulate PCE emissions from dry cleaning facilities. EPA classifies all sources in the industrial dry cleaning category as major sources. For the purposes of the rule, a major source includes any source emitting more than ten tons of PCE per year. Sources in the commercial dry cleaning sector may be major or area sources (i.e., sources where potential emissions do not exceed ten tons per year, considering controls). Sources in the coin operated dry cleaning sector are exempt from the standards. The standards require all new and existing dry cleaning facilities that are major sources of PCE to control emissions to the level of maximum achievable control technology. New and existing area sources must control PCE emissions to the level achieved by generally available control technologies. Table 10.2 summarizes the requirements of the PCE Dry Cleaning NESHAP (58 FR 49354). Dry cleaners had until June 20, 1994 to meet reporting requirements of the PCE NESHAP (58 FR 66287).

In announcing the rule, EPA said that dry cleaners doing less than $75,000 in business annually will be exempt from some of its major controls.[19] EPA estimated that the NESHAP will

cut process vent emissions of PCE by about 7,300 tons per year and fugitive emissions by about 28,400 tons per year.[20]

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

Recent studies have raised new concerns about the potential for exposure to PCE from dry cleaning facilities. Elevated concentrations of PCE have been found in indoor air at dry cleaning establishments and at apartments situated above dry cleaning establishments.

Worker safety is a significant concern in the dry cleaning industry. In January, 1989, OSHA adopted a 25 ppm PEL for PCE to reduce the health effects from worker exposure to PCE. OSHA allowed a four year phase-in period for complying with the PEL "by any reasonable combination of engineering controls, work practice, and personal protective equipment effective September 1, 1989 through December 30, 1992."[21] After the transitional period, OSHA requires the PEL to be achieved without personal protective equipment.

PCE emissions from dry cleaning also contribute to toxic air pollutants in the environment. Low levels of PCE have been detected in the atmosphere. Higher concentrations have been detected in urban areas that contain numerous dry cleaning point sources. For example, the average distribution of PCE in air in the northern hemisphere was 56 parts per trillion in 1978. Typical levels of PCE in ambient air in urban or industrial areas range from 0.3 to 1.5 parts per billion (ppb) and may reach 10 ppb or higher.[22]

In Germany, a study was conducted to evaluate PCE air pollution originating from coin operated dry cleaning establishments. The study found indoor air concentrations of PCE between 3.1 and 331 mg/m^3 at the dry cleaning

TABLE 10.2   REQUIREMENTS OF THE PCE DRY CLEANING NESHAP

Requirement	Small area source	Large area source	Major source
Applicability: Dry Cleaning Facilities with:			
(1) Only Dry-to-Dry Machines...	Consuming less than: 140 gallons PCE/year...	Consuming between: 140-2,100 gallons PCE/year	Consuming more than: 2,100 gallons PCE/year
(2) Only Transfer Machines...	200 gallons PCE/year...	200-1,800 gallons PCE/year	1,800 gallons PCE/year
(3) Both Dry-to-Dry and Transfer Machines...	140 gallons PCE/year...	140-1,800 gallons PCE/year	1,800 gallons PCE/year
Process Vent Controls:			
Existing Facilities...	None......	[a]	[a]
New Facilities...	[b]	[b]	Refrigerated condenser followed by small carbon adsorber (or equivalent)
Fugitive Controls:			
Existing Facilities...	[c] [d] [e] [f] [g]	[c] [d] [e] [f] [g]	Room enclosure
New......	......	......	

Source:
Federal Register, Vol. 58, No. 182, September 22, 1993.
[a] Refrigerated condenser (or equivalent). Existing carbon adsorbers can remain.
[b] Refrigerated condenser (or equivalent).
[c] Leak detection/repair.
[d] Store all PCE solvent and waste in sealed containers.
[e] Leak detection/repair.
[f] Store all PCE solvent and waste in sealed containers.
[g] No new transfer machine systems allowed.

establishments. Air samples collected from a private car, in which a freshly cleaned jacket had been transported, contained 9.3 mg/m³ PCE two minutes after the jacket was placed in the car, and 20.4 mg/m³ after the car had been driven and parked. The study also found concentrations of PCE in butter in apartments over the dry cleaning shops.[23]

Recently, a study of indoor air in apartments situated above dry cleaning establishments was conducted by the New York State Department of Health. PCE levels ranged from 300 to 55,000 μg/m³, with the highest concentrations found in residences located above dry cleaners using transfer machines. Elevated levels of benzene and toluene were detected at one residence. The study also found elevated concentrations of PCE in outdoor air near the dry cleaning facilities.[24]

Depending on the size of the facility and the waste generation rate, the solid wastes containing PCE generated at a dry cleaning facility may be regulated as a hazardous waste under RCRA. Facilities typically drain, recover, and reuse PCE from spent carbon filters prior to disposal. Thus, the amount of PCE remaining in the waste is reduced. PCE contaminated waste is typically carried off-site periodically by a hazardous waste collection firm.

EVALUATION OF SAFE SUBSTITUTES FOR PCE IN DRY CLEANING

Safe substitute approaches to reducing the use of PCE in dry cleaning include the following:

■ reducing the use of water-sensitive fabrics and garments that require dry cleaning;

■ modifying the professional cleaning process to eliminate or reduce the use of organic solvents; and

■ substituting a safe solvent for PCE in current dry cleaning processes.

Each of these approaches are discussed below.

Reducing the Use of Water-Sensitive Fabrics

As discussed in the introduction, dry cleaning is used on fabrics that are subject to shrinkage or other adverse effects from aqueous cleaning. One alternative to dry cleaning is to develop fabrics that are not sensitive to water, such as washable silks and rayons. In recent years, washable silks and rayons have been developed that do not require professional cleaning. Other innovations in fabric technology include the introduction of wrinkle-free cottons. Although dry cleaning is primarily needed for clothing that cannot be effectively laundered at home, a growing percentage of new clothing is launderable.[25]

A similar alternative is to select garments made of fabrics not sensitive to water instead of garments made from water-sensitive fabrics. Historically, industrial laundry facilities have used both dry cleaning and water-based cleaning equipment. The proportion of facilities that use aqueous or dry cleaning changes with the changes in relative economics or in the garment type chosen by the customer.[26] Industrial dry cleaning plants are moving away from dry cleaning and toward aqueous cleaning,[27] perhaps because of new, costly regulations, and the potential liability that could result from spills, leaks, or accidental worker exposure to high levels of hazardous chemicals.

> *The professional garment cleaning process has changed little over the years. Increasing concern about the potential health and environmental effects of PCE, however, has engendered new interest in alternative processes.*

Alternative Cleaning Processes

Currently there are no alternative professional cleaning processes that provide the same function as dry cleaning in widespread use in the U.S. In recent years, however, increasing attention has been given to the development or evaluation of alternative cleaning processes. Potential

alternatives include multiprocess wet cleaning, nitrogen injection of petroleum solvent, oxygen vacuum with petroleum solvent, supercritical carbon dioxide, machine wet cleaning, microwave drying, and ultrasonic agitation.

Multiprocess wet cleaning and machine wet cleaning are two new methods that use water as the primary cleaning solvent. The nitrogen injection and oxygen injection methods seek to reduce the flammability hazard of petroleum-based methods by lowering the oxygen concentration in the cleaning drum. These alternative processes are not considered safe substitutes within the context of this report since they may result in the use and release of the 33/50 aromatics. Microwave drying and ultrasonic agitation are two processes still under development. Two of these potential alternative cleaning processes, multiprocess wet cleaning and a proposed ultrasonic agitation system, are described below.

Multiprocess Wet Cleaning. Multiprocess wet cleaning, as defined by EPA, is a series of textile cleaning steps which include spotting and wet cleaning, with predominantly water-based cleaning solutions which are usually not recovered for reuse.[28] ECOCLEAN® International, Inc. is a commercial vendor and franchiser of a multiprocess wet cleaning method that has been used commercially in the United Kingdom for a number of years.

The ECOCLEAN® process assumes that almost 80 percent of fabrics can be cleaned by washing or wet cleaning. Washing is the immersion of fabrics in water either by using a washing machine or by hand. Wet cleaning involves the localized application of water, steam, and soap. According to the company literature, fabrics that cannot be washed or wet cleaned can still be adequately cleaned with the ECOCLEAN® process.

The basic ECOCLEAN® process relies on cold water-based soaps made from essential oils, hand spotting to remove oily stains, and steam to clean bacteria. An anti-static conditioner is used to penetrate the fabric and release insoluble soils. The company literature compares the ECOCLEAN® process for cleaning a man's suit to the traditional dry cleaning method. The comparison is shown in Table 10.3

The ECOCLEAN® process differs from traditional dry cleaning in that it does not use chlorinated solvents, it is more labor intensive, and it relies heavily on the skills of the spotter. The company claims that increased labor costs are balanced by decreased solvent costs and energy consumption. Equipment requirements for the ECOCLEAN® process are similar to those of the dry cleaning process, and extensive modification of existing equipment is typically not required to convert to the ECOCLEAN® process.[29] No information was available on the

TABLE 10.3   COMPARISON OF CLEANING METHODS

ECOCLEAN® Method	Solvent Dry Cleaning Method
Inspect for stains Hand spot as required Tumble dry Vacuum to remove insoluble soil Reinspect for stains Press with live steam	Inspect for stains Hand spot as required Dry Clean Reinspect for stains Press with live steam

Source:
ECOCLEAN®

actual costs for converting a typical commercial dry cleaning establishment to the ECOCLEAN® system.

From the company's perspective, the main barrier to the use of the ECOCLEAN® process is public perception.[30] People believe dry cleaning is necessary to clean water-sensitive fabrics. In addition, garment care labels in the U.S. are only required to provide one recommended method for cleaning a garment. Frequently, dry cleaning is recommended when washing or wet cleaning would be as effective since there is less potential for damage with professional garment care.

The EPA Design for the Environment (DfE) Program, in collaboration with ECOCLEAN® International, Inc., the International Fabricare Institute, the Massachusetts Toxics Use Reduction Institute, and the Neighborhood Cleaners Association, recently conducted a cost and performance comparison of conventional dry cleaning and the ECOCLEAN® method of multiprocess wet cleaning. The results of the study showed that in certain situations, the multiprocess wet cleaning process is technically feasible and economically competitive with conventional dry cleaning. The DfE Program will evaluate the risks of the wet cleaning and other alternative processes in a Cleaner Technologies Substitute Assessment (CTSA).

Ultrasonic Agitation. One proposed, but undemonstrated alternative garment cleaning system would use the ultrasonic agitation of constrained clothing in an aqueous, continuous flow process. The proposed system is based on the following premises:

- water combined with surfactants, wetting agents, and oxidizers is the preferred solvent for cleaning clothes;

- ultrasound can be used to provide the agitation of the traditional cleaning drum;

- constraining the garments will increase the efficacy of the ultrasound by making garments more closely resemble a solid surface thus decreasing their potential to absorb energy;

- constraining the garments will preclude shrinkage;

- since a press is defined as the position and shape a fabric is in when moisture (usually steam) is removed, constraining the garments will result in a "pressed" look in the drying stage; and

- a continuous flow, conveyorized system will allow for more efficient processing than current batch-style equipment.

Thus far, preliminary tests on the effects of porous lateral constraint on shrinkage and the garment finishing process (i.e., pressing) have been conducted. Test results show that porous lateral constraint can control shrinkage on certain fabrics and can be used to impart a "pressed look" to fabrics. The DOE's Kansas City facility is collaborating with Garment Care on these tests.

Since a growing percentage of new clothing is home launderable, industry growth potential is seen as slim to negative. Besides the environmental advantages, a fundamental goal in developing this alternative process is to make the professional garment cleaning process more efficient and economically competitive with home laundering.[31]

Solvent Substitutes

There are only a limited number of organic solvents currently used for dry cleaning. The dry cleaning solvents with the largest market shares are PCE and petroleum blends. Chlorofluorocarbon-113 (CFC-113) and TCA are also used to a lesser extent. Although they are not considered a "safe" substitute in the context of this report, petroleum blends were evaluated as possible substitutes for PCE and TCA. Much of the recent research in solvent substitutes has been aimed at reducing the flammability hazard of petroleum blends used in dry cleaning. CFC-113 is not considered a potential safe substitute since this chemical causes ozone depletion and is being phased-out of production.

Petroleum Solvents. Petroleum solvents such as Stoddard Solvent have a 10 to 12 percent share of the dry cleaning market in North America.[32] A major use of petroleum solvents is leather and suede cleaning. The relatively gentle solvency of petroleum blends makes petroleum solvents popular for a range of textile garments as well. There are several barriers to the use of petroleum solvents as safe substitutes for PCE, however.

The primary barrier to using petroleum blends in broad range dry cleaning application is their flammability. Frequently, local insurance, zoning, and safety considerations favor a solvent substitute that is nonflammable. PCE was first widely used as a safe substitute for petroleum blends because it is nonflammable. The recently introduced nitrogen injection and oxygen vacuum dry cleaning equipment are designed to reduce the flammability hazard of petroleum solvents by limiting the availability of oxygen in the cleaning drum. Another petroleum blend, called 140°F Solvent, is similar to Stoddard Solvent, except it is less flammable.

A second obstacle to using petroleum blends is costly liability insurance requirements for commercial facilities that store petroleum products in underground storage tanks (UST). EPA UST regulations require facilities that store petroleum in USTs and have a throughput of 10,000 gallons per year or more to obtain $1 million of liability insurance. Facilities with a throughput of less than 10,000 gallons per year are required to obtain $500,000 of liability insurance. One industry representative believes that the typical commercial dry cleaning shop owner would be unable to absorb this added cost and remain cost-competitive.[33]

Third, petroleum blends are not "drop-in" replacements for PCE. Switching a PCE-based dry cleaning facility to a petroleum-based facility would require equipment modifications, particularly in the distillation equipment. Many facilities that use PCE have recently modified or replaced their existing PCE-based equipment in an effort to meet the OSHA PEL for PCE. An

industry representative suggested that anything that affects the availability or price of PCE, or requires additional equipment modification would be a major blow to the industry because of the money recently invested in new equipment or equipment modifications.[34]

Finally, petroleum blends contain toxic chemicals. Data on the potential for exposure and health effects of exposure to petroleum blends would be required to determine if use of these chemicals results in less risk to workers or others. The EPA Office of Pollution Prevention and Toxics (OPPT) through its DfE Program is collaborating with industry to develop a CTSA for the dry cleaning industry. The CTSA will examine the trade-offs in risk, performance, and cost of alterative solvents or professional cleaning processes that can be used in place of the traditional dry cleaning process.

Other Substitute Solvents. Producers of CFCs were making efforts to identify other solvents, such as HCFCs, that could be substituted for CFC-113, but one industry contact was unaware of any large scale effort to find a substitute for PCE. The efforts to find a substitute for CFC-113 reportedly have been terminated, possibly due to the relatively small amount of this solvent that the dry cleaning industry uses.[35]

At least one firm that manufactures so-called "environmentally friendly products" has advertised an environmentally safe, all natural alternative to dry cleaning.[36] The manufacturer claims that the product is a blend of non-toxic natural plant oils that removes light soil and odors, but not stains. The manufacturer claims that the plant oils work by breaking the bonds between the clothing and the soil and odors. The soil and odors are encapsulated by the natural plant oils, which are then vented through the dryer.

Consumers use the product by spraying it directly onto lightly soiled or odor laden clothing and drying them in the home dryer for two minutes. The Material Safety Data Sheet (MSDS) for the product indicates that it contains

no hazardous ingredients and has no flashpoint. No attempt was made to evaluate the efficacy of this product.

Conclusions

After decades of using a well established and accepted batch process of cleaning clothes with solvents, substantial progress has been made recently in reevaluating the dry cleaning process to identify technically and economically feasible safe substitute processes. It appears, however, that little or no efforts are underway to identify safe chemical substitutes for PCE in the

traditional dry cleaning process, and this study was unable to identify any existing safe substitutes. The most promising course to eliminate or significantly reduce the use of PCE for this application appears to be the use of more washable fabrics, or the adoption of an alternative cleaning process. Recent efforts by the industry to meet EPA and OSHA regulations, however, have probably made the industry sensitive to changes that would require more capital investment. More research is needed to develop and demonstrate some of the proposed alternative processes.

ENDNOTES

[1] *Federal Register*, US EPA, December 9, 1991, p. 64383-64386.

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[3] *Federal Register*, US EPA, December 9, 1991, p. 64383-64386.

[4] *Survey of Perchloroethylene Emission Sources*, US EPA, Office of Air Quality, (Research Triangle Park, NC, May 1985).

[5] Ibid.

[6] *Federal Register*, US EPA, December 9, 1991, p. 64388.

[7] *Survey of Perchloroethylene Emission Sources*, US EPA, Office of Air Quality, (Research Triangle Park, NC, May 1985).

[8] *Federal Register*, US EPA, December 9, 1991, p. 64387.

[9] *Survey of Perchloroethylene Emission Sources*, US EPA, Office of Air Quality, (Research Triangle Park, NC, May 1985).

[10] Ibid.

[11] *Federal Register*, US EPA, December 9, 1991, p. 64383.

[12] "Chemical Profile: Perchloroethylene," *Chemical Marketing Reporter*, January 20, 1992.

[13] *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., (Weinham: VCH Verlag., 1985), Vol. A9.

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[16] *Survey of Perchloroethylene Emission Sources*, US EPA, Office of Air Quality, (Research Triangle Park, NC, May 1985).

[17] Ibid.

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[19] *Environmental Reporter*, September 17, 1993.

[20] *Environmental Reporter*, September 24, 1993.

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[25] Conversation with David Porter, Garment Care, April 27, 1994.

[26] *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., (Weinham: VCH Verlag., 1985), Vol. A9.

[27] *Federal Register*, US EPA, December 9, 1991, p. 64386.

[28] *Multiprocess Wet Cleaning: Cost and Performance Comparison of Conventional Dry Cleaning and An Alternative Process*, US EPA, Pub. No. 744-R-93-004, Office of Pollution Prevention and Toxics, September 1993.

[29] *Subject: Clothes Care Alternative to Chlorinated Solvent Dry Cleaning*, ECOCLEAN®, (London).

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Fast Laundry, November 12, 1993.

[32] *Ullmann's Encyclopedia of Industrial Chemistry*, 5th ed., (Weinham: VCH Verlag., 1985), Vol. A9.

[33] Conversation with Mohammed Kamara, International Fabricate Institute, May 26, 1992.

[34] Conversation with Dr. Jerry Harlan, ADCO, May 26, 1992.

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[36] *Environmentally-Safe All Natural Dry Cleaning Alternative Introduced by Natural World: Dry Clean in Your Dryer*, Natural World, Inc., (Stanford).

CHAPTER 11

PAINT STRIPPING

Chemical paint stripping formulations that include the 33/50 chemical dichloromethane (DCM) are widely used by industry and the public to remove paints and coatings from a substrate. This use of DCM is of particular concern because it can result in both consumer exposure and worker exposure to this toxic 33/50 chemical. Recently, several safe substitutes for DCM-based paint strippers have been developed. This chapter describes the use of and substitutes for DCM.

PRODUCT PROFILE

Paint strippers are used in both industrial and consumer applications. Industrial applications include the manufacturing of automobiles, of metal and wood furniture, and the maintenance of aircraft and military equipment. In the consumer market, paint strippers are primarily used to strip off old paint or varnish from household products such as furniture.

Paint strippers are classified as application strippers or immersion strippers. Application strippers commonly have a solvent base and are usually applied by brushing or spraying directly onto the substrate. Common for small consumer jobs, these paint strippers are also used in industrial applications.

Immersion strippers are used primarily in industrial applications to strip numerous items simultaneously. Immersion types use either solvent-based or aqueous baths. Solvent-based baths, also called cold baths, are the most widely used by industry. Aqueous paint strippers, also called hot baths, include caustic or acid products. Caustic strippers, the most widely used of the aqueous paint strippers, are operated at temperatures ranging from 82 to 116°C. They contain caustic soda as the primary paint stripping agent, chelating agents, and up to 20 percent organic solvents.[1]

> *The use of DCM-based paint strippers can result in both consumer and worker exposure to this toxic 33/50 chemical. Health and safety concerns have helped spawn the development of a number of safer substitutes for DCM-based products.*

Although caustic cold baths may contain a small fraction of DCM in their formulation, they are not the focus of the substitutes assessments presented here. Instead, this chapter focuses on the use of and substitutes for cold bath immersion strippers and application strippers that use DCM as the key ingredient.

Quantity of DCM Used in Paint Stripping

About 124 million pounds, or 31 percent of the total annual consumption of DCM, was used for paint stripping in 1991.[2] Of this total, 40 percent is used in industrial applications such as periodic maintenance of commercial and military airplanes, automobiles, and other equipment. Another 40 percent is used in consumer applications for the stripping of old finishes from furniture and other wood. The remaining 20 percent is used for cleaning and reworking in the manufacturing of automobiles and other industrial goods. Approximately two-thirds of the DCM used in the consumer market is used directly by a home hobbyist. The other one-third is used in the commercial submarket, where a contractor performs the coating removal job.[3]

Price of DCM Used in Paint Stripping

In January, 1994, the price for large volumes of industrial grade DCM was $0.29 per pound. In April, 1994, prices of DCM-based paint stripping formulations prepared for the consumer market and sold in the Knoxville, Tennessee area ranged from about $13 to $20 per gallon (about $2 to $3 per pound). The amount of coverage provided by DCM-based paint strippers varies from about 50 to 100 square feet per gallon.[4]

DESIRED PROPERTIES OF CHEMICAL PAINT STRIPPERS

The selection of a paint stripper depends on the substrate, type of coatings to be stripped, available equipment, time and temperature limitations, odor and flammability of the stripper, and disposal requirements for the spent stripper. The desired properties of paint stripping formulations include low flammability, water solubility, low molar volume, low surface tension, and relatively low odor and low fumes.

Paint strippers should have low flammability for safer application in potentially hazardous locations such as the paint mix room and spray booths.[5] Water soluble solvents are easier to rinse from the substrate. A low-molar-volume paint stripper allows fast and efficient solvent penetration of the cured paint or coating. Low surface tension allows the solvent to quickly cover the entire surface being stripped and allows immediate penetration of the paint film. A paint stripping solvent with relatively low odor and low fumes reduces the chance of respiratory problems or asphyxiation.[6]

DCM-based paint strippers have found wide acceptance because of their effectiveness and efficiency, their applicability to a wide variety of substrates and coatings, and their relatively low cost. DCM is nonflammable and nonexplosive when mixed with air. It is also the fastest of the chlorinated solvents in lifting paint film.[7]

PROCESS DESCRIPTIONS

DCM-based paint strippers may contain a number of components. The following sections present typical composition ranges for DCM-based strippers and the process for manufacturing them; the paint stripping method used during consumer applications; and solvent-based industrial paint stripping methods.

Manufacturing of DCM-Based Paint Strippers

Components of a DCM-based stripper may include co-solvents, activators, corrosion inhibitors, evaporation retarders, thickeners, emulsifiers, and wetting agents. Each of these components provides particular functions. Co-solvents, usually alcohols, esters, glycol ethers, aromatic solvents, or ketones, are added to the

formulation to increase the versatility of the remover in attacking coatings. Activators, such as ammonia, amines, and formic acid, are included to increase the rate of stripping. Evaporation retarders, such as paraffin wax, are used to form a film on the surface and slow evaporation. A cellulosic thickener may be added to hold the stripper on vertical surfaces.

DCM-based paint strippers are formulated by mixing the components according to a predetermined order of addition. Mild heat is sometimes used to dissolve paraffin wax if it is used as an evaporation retarder.

DCM-based paint strippers formulated for consumer use may be classified according to their flammability. Nonflammable paint strippers contain 75 percent or more of DCM, and 5 to 15 percent of methanol, ethanol, isopropanol, or a combination of the three. Flammable DCM-based paint strippers contain about 15 to 20 percent of DCM, 20 to 25 percent of methanol, 35 to 40 percent of toluene or mineral spirits, and 20 to 25 percent of acetone.[8]

Typical composition ranges for DCM-based strippers are listed in Table 11.1. The concentration of DCM in existing paint strippers may vary significantly, particularly in the consumer market.

Consumer or Household Paint Stripping

Furniture stripping accounts for about 85 percent of the consumer use of paint strippers.[9] The method for stripping off old paint with chemical strippers requires very little equipment. The paint stripper is brushed or sprayed in one direction onto the surface, two square feet at a time. The resulting sludge is removed by gently scraping with a dull putty knife. After the sludge is removed, residue is wiped away with mineral spirits or some other solvent.

Industrial Paint Stripping

Industrial paint stripping methods are used in OEM and maintenance services. In OEM industries, paint strippers are required to perform the following: 1) strip defective manufactured goods before repainting; 2) clean overspray from painting equipment like spray booths, hooks, hangers, and racks; and 3) purge paint lines and spray guns.

In maintenance services, paint stripping plays an important role in repainting commercial automobiles and aircraft. Here, the paint stripper is either sprayed or brushed onto the surface of the vehicle, or the parts are immersed into a cold bath containing DCM. After the solvent softens the paint, it is removed by mechanical scraping.

TABLE 11.1   COMPOSITION OF NONFLAMMABLE DCM-BASED PAINT STRIPPERS

Component	Percent by Weight
Alcohol (e.g., Methanol, Ethanol or Isopropanol)	5 to 10
Amine (e.g., Dimethylethanolamine)	1
DCM	70 to 85
Hydrocarbon Solvents or Ketones	0 to 10
Methyl Cellulose (Thickeners)	1 to 2
Paraffin Wax	1 to 3
Surfactants/Emulsifiers	3 to 6

Source:
Kirk-Othmer Encyclopedia of Chemical Technology, 1978

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ENVIRONMENTAL RELEASES OF DCM FROM PAINT STRIPPING

Environmental releases from the use of DCM in paint stripping formulations occur from the production of DCM through the paint stripping process and the final disposal of DCM residuals. The following sections present the environmental releases from production and distribution of DCM, followed by the releases from the actual stripping process.

Environmental Releases from Production and Distribution of DCM

Emissions from DCM production facilities reported in the 1991 TRI were discussed in Chapter 3. Total environmental releases and off-site transfers of DCM from production facilities in 1991 were 0.93 million pounds. Using the principles of life cycle assessment, if 31 percent of the DCM produced in the U.S. is consumed in paint stripping formulations, approximately 31 percent of these releases can be associated with DCM produced for this use. Similarly, some of the DCM emissions from distribution facilities are associated with DCM distributed to manufacturers of paint stripping formulations.

Almost all of the DCM produced is distributed through distribution facilities. Distribution facilities are not required to report their emissions in the TRI, but in 1983 it was estimated that more than one million pounds of DCM were emitted to the atmosphere from these facilities.[10]

Environmental Releases of DCM from Paint Stripping

Environmental releases of DCM that are directly associated with the paint stripping industry include releases from manufacturers of DCM-based paint strippers and releases from the actual paint stripping process.

Companies that manufacture paint stripping formulations are classified under the SIC code number 2851 (paints and allied products manufacturers) and are required to report emissions in TRI. The emissions of DCM for

SIC 2851 reported in the 1991 TRI are shown in Table 11.2. Almost 600,000 pounds of DCM were reported released from paints and allied products manufacturers in 1991. Most of these releases (59 percent) were emitted on-site to the air. The remaining 41 percent was transferred off-site to POTW or treatment, storage, and disposal facilities. These release figures may also include emissions from facilities that prepare other types of paints and allied products that use DCM.

EPA emission factors for the paint stripping process range from a low of 400 pounds per ton of DCM contained in the stripper formulation to a high of 2,000 pounds per ton of DCM (100 percent loss to the atmosphere). The lower emission factor is for dip tanks at durable good manufacturers with emissions controlled by a water seal and a 15 second drain time. The higher emission factor applies to uncontrolled emissions from floor stripping, furniture stripping, and other general sources.[11]

> *EPA estimates that all of the DCM used in consumer-oriented paint stripping products is released to the atmosphere. Consumer exposure to DCM via inhalation may result in acute or chronic health effects.*

HEALTH, SAFETY, AND ENVIRONMENTAL ISSUES

The main exposure to DCM from paint stripping occurs from inhalation. The health effects of acute inhalation exposure discussed in Chapter 3 include CNS depression and elevated carboxyhemoglobin levels in the blood. The consumer use of DCM-based paint strippers can result in elevated carboxyhemoglobin levels that could stress the cardiovascular system to intolerable levels in a person with a diseased CNS. DCM was considered the primary agent responsible for the death of a 13 year-old boy who was using a DCM paint remover.[12]

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TABLE 11.2   RELEASES AND TRANSFERS OF DCM FROM THE PAINTS AND ALLIED PRODUCTS INDUSTRY
(SIC 2851)

Chemical	Releases and Transfers (lbs/yr)							
	Air Release	Water Release	Land Release	Underground Injection Release	Total On-Site Releases	POTW Transfer	Other Off-Site Transfer	Total Off-Site Transfers
DCM	349,168	7	5	0	349,180	140,944	104,594	245,538
TOTAL	349,168	7	5	0	349,180	140,944	104,594	245,538

Sources:
TRI, 1991
Correspondence from Hampshire Research Assoc., Inc.
U.S., EPA, Office of Pollution Prevention and Toxics, 33/50 Program Office

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EPA has assigned DCM a B2 carcinogenicity rating based on positive evidence of carcinogenicity in animal studies.

Because of these health concerns, OSHA has proposed lowering the permitted average hourly industrial exposure to DCM from 500 ppm to 25 ppm.[13] Monitoring data suggest that the mean time-weighted average personal exposure to DCM in the workplace may be 100 to 200 ppm or higher during paint stripping operations.[14] Industry believes that the OSHA proposal could accelerate declines in some segments of the DCM market, particularly in paint stripping applications.[15] Still, consumers using DCM-based paint strippers are afforded little protection beyond warning labels on the product container.

EVALUATION OF SAFE SUBSTITUTES FOR DCM PAINT STRIPPERS

In recent years, several alternatives to DCM-based paint stripping formulations have been developed. In the industrial sector, these include:

- alternative paint stripping methods, such as media blasting technologies;

- alternative chemical formulations that do not use DCM; and

- product or process modifications that reduce or eliminate the need for paint stripping.

In the consumer sector, safe substitutes for DCM-based paint strippers are primarily alternative chemical formulations that attempt to use less toxic chemicals.

The substitutes assessments in this chapter focus on the use of media blasting technologies and process modifications in the industrial sector, and the use of alternative chemical formulations in the consumer market. Except for economic data, most of the information on alternative chemical formulations is also applicable to the industrial sector.

Media Blasting Technologies

Several paint stripping methods are available that involve blasting the substrate with dry or liquid media. These methods, characterized as dry blasting or wet blasting, are usually used to remove paint from airplanes and other vehicles. In wet blasting, a liquid media is used (e.g., high pressure water spray, crystalline ice, and sodium bicarbonate), whereas dry blasting employs soft plastic, wheat-starch, or carbon dioxide dry ice as the blasting media.

Bicarbonate Media Blasting. The bicarbonate media blasting method is a low impact blasting technology and a safe, cost-effective alternative. This process utilizes low-pressure blasting equipment with a specially formulated abrasive media based on sodium bicarbonate. Bicarbonate media blasting can be used in airplane maintenance, industrial equipment maintenance, and OEM industries.

Sodium bicarbonate, more commonly called baking soda, is water soluble, nonflammable, nonexplosive, nonsparking, and nontoxic. The sodium bicarbonate-based blasting system is capable of removing paint as well as grease and oil. The method is applicable to virtually any substrate, particularly thin skinned metal and composite substrate.

Industrial users of DCM-based paint strippers can substitute alternative paint stripping formulations or methods; or they can modify their products or processes to reduce or eliminate the need for paint stripping. Currently, the most viable option for consumers is to use alternative chemical formulations.

Bicarbonate media blasting involves propelling the media by compressed air onto the surface to be cleaned. The media strikes the surface and disintegrates, taking with it the coating. High pressure water is injected to reduce the dust generated. The spent media is not reusable for paint stripping but may be used in a waste treatment facility to increase the

alkalinity of other wastestreams. However, some contaminants of waste paint are hazardous to humans and the environment. Proper treatment of wastewater, therefore, is essential prior to disposal.

One of the disadvantages of this method is that sodium bicarbonate may revert to caustic soda ash in the presence of water and heat. The hydrophilic nature of the soda ash can result in the absorption of small amounts of moisture from the air, which could cause corrosion problems. Reportedly, it would be difficult to protect an airplane from bicarbonate media intrusion. Thus, the Federal Aviation Administration (FAA) has not approved bicarbonate media blasting for stripping aircraft. The total stripping cost for this method has been estimated at $3.51 per square foot.[16]

Plastic Media Blasting. The plastic media blasting method of dry paint stripping utilizes a manufactured soft plastic media. Urea is the most widely used resin in plastic media blasting, accounting for 60 percent of the market in 1992. Other materials used include melamine, acrylic, clear-cut or polyester, although polyester is rarely used today because it's stripping action is too slow. The raw stock for most plastic media is scrap molded parts, but some media manufacturers also buy virgin molding compounds and mold plates specifically for plastic media blasting.[17] After use, plastic media can be recycled, cleaned, and regraded to virgin media standard.

Plastic media blasting requires precision control of media flow rates, particle ejection velocity, and air pressure. Equipment requirements include a blasting machine and an air compressor for a supply of clean, dry compressed air. The abrasive plastic beads are forced at high velocity through a nozzle at the painted surface; the resulting impact dislodges the paint.

Waste is generated by the dislodged paint and the breakdown of the plastic beads. Therefore, a dust collecting and separating system is required. The separated waste paint is treated prior to disposal. This dry paint stripping method has the benefit of producing less wastewater.

Problems associated with plastic media blasting include pitting or warping of the substrate, low cutting rate, high media breakdown rate, dust, and static. Plastic media blasting is not believed to have universal application for aerospace coating removal because the process is too aggressive for aluminum and composite surfaces.[18]

Many of the problems with plastic media blasting have been associated with the materials used to manufacture the media or the grinding and classifying process. For example, scrap molded parts used to make blasting media may have been scrapped because of poor cure in the molding process; excessive flash (partially cured material on finished moldings at the junction of the upper and lower molds) on the moldings; or they contain contaminants. Blasting media made from such scrap parts can be too soft or of inconsistent quality. Blasting media made from virgin materials, however, can also be made from source materials of variable quality, leading to similar problems of inconsistent quality.[19] Despite these potential problems, the method has been successfully used in a number of operations and is approved by the FAA.[20]

The U.S. Navy has compared the process costs for chemical paint stripping and plastic media stripping of aircraft. Included in the cost figures are material cost (chemicals or plastic media), labor cost, utility costs, waste treatment and disposal costs, and equipment maintenance costs. Even without considering indirect costs such as reduced liability cost, the Navy estimated that plastic media blasting would save about 49 percent of the cost of chemical paint stripping, from $25,898 per plane for chemical stripping to $13,316 per plane for plastic media stripping.[21]

Starch-Based Media Blasting. The starch-based media blasting method employs a dry blast media manufactured from high quality wheat starch in crystalline form. The wheat starch product does not contain toxic chemicals and is nonexplosive. Starch-based media blasting is used to remove coatings in the aerospace industry, particularly polyurethane and epoxy paints from aluminum and composite surfaces. In addition, it is capable of removing paint in

other industrial applications, such as equipment and mold cleaning.

Disposal of the waste generated in this method depends on the toxicity of the coatings. In small scale operations, the spent dust generated from the dry-blasting media is removed from the work area by a cyclone device.

Negative qualities of starch-based media blasting include slower paint stripping rates than with plastic media, and high cost. Starch moisturization presents another problem; once the starch is wet, it will no longer be effective for stripping, even if dried. As a result, a clean, dry air supply for the blast stream and measuring equipment is recommended to prevent the accumulation of moisture. The total stripping cost for this method has been estimated at $1.87 per square foot.[22]

Starch-based media blasting is reportedly able to strip a wide range of coatings from graphite, fiberglass, and Kevlar without the risk of damage to the substrate associated with plastic media blasting. Commercial airlines are now using wheat starch blasting to remove polyurethane paints from thin clad aluminum in selected applications. The U.S. military is also reportedly evaluating wheat starch as a blasting media.[23]

Other Media Blasting Technologies. Other media-blasting methods include carbon dioxide dry ice blasting, high-pressure water blasting, and crystalline ice blasting. Carbon dioxide dry ice can be used as a blasting media, but, like sodium bicarbonate media blasting, is not approved by the FAA for airplane maintenance. Negative qualities of carbon dioxide dry ice include its low productivity and its possible contribution to global warming, albeit small.

High pressure water blasting may be employed on some substrates, but is ineffective against polyurethane coatings without first applying a chemical stripper. The high-pressure water blast may also pose a danger to workers, and treatment of the process water is required before being released to the sewer.

Crystalline ice blasting has been evaluated by the FAA. It does not remove aerospace coatings. Furthermore, this ice blasting method requires refrigeration, ice-making, and ice-handling equipment as well as protection from excessive noise.[24]

Chemical Substitutes

Safe chemical substitutes are the most viable alternative for the consumer market since they do not require costly equipment. A number of chemicals have been proposed or used as substitutes for DCM in paint strippers. These include NMP, DBEs, paint thinners, and other solvents (e.g., alkyl acetate, diacetone alcohol, and glycol ethers). Generally, chemical substitutes have not been proven as effective in paint stripping as DCM, especially on aged paint. Also, the toxicity of chemical substitutes may not be well documented.

As the solvents most frequently used in alternative paint strippers formulated for the consumer market, this section focuses on NMP and DBEs and their relative performance, cost, and environmental attributes as compared to DCM. It should be noted, however, that products containing these solvents and advertised as safe may contain other toxic chemicals, such as petroleum hydrocarbons. Researchers in Denmark have found that chemical products containing petroleum fractions may contain trace levels of benzene. They measured the benzene content in paint strippers and other chemical products in which petroleum fractions are used as ingredients and found benzene concentrations of 4 to 748 ppm.[25]

Frequently, consumers cannot identify all of a product's toxic ingredients from the product label. For example, the MSDS from one product that contains NMP and a DBE indicates that the product also contains 8 to 15 percent mixed petroleum hydrocarbons. The only chemical ingredients listed on the label are "esters of nonbasic acids" (DBEs).

DBE-based paint strippers formulated for the consumer market cost approximately $20 per gallon; NMP-based paint strippers are about $35 per gallon. Coverage for non-DCM formulations is generally 15 to 25 square feet per gallon as compared to 50 to 100 square feet for DCM products.[26] DCM-based paint strippers

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only remove one layer of paint at a time, where the non-DCM formulations can strip multiple layers in one application.

N-Methyl Pyrrolidone. NMP is an acetylene-based solvent with lower density than DCM. It is produced by the reaction of butyrolactone with methylamine or from the high-pressure synthesis of acetylene and formaldehyde.[27] Manufacturers of NMP include ARCO Chemical Company in Channelview, Texas; BASF Corporation, Chemical Division in Geismar, Louisiana; and GAF Building Materials, a subsidiary of International Specialty Products, Inc. in Calvert City, Kentucky and Texas City, Texas.[28] Annual production volume exceeds 55 million pounds. EPA estimates that approximately 2.7 million consumers and more than 71,000 workers may be exposed to NMP.[29] Releases and transfers of NMP were not required to be reported in the 1991 TRI.

Besides its use in paint stripping formulations, NMP is used as a pigment dispersant, in petroleum processing, as a chemical intermediate, and as a spinning agent for polyvinyl chloride. NMP is used in pharmaceutical applications to enhance the penetration and transfer of substances through the skin. It has also been approved as a solvent for slimicide application to food packaging materials.[30]

NMP-based paint strippers are generally formulated at lower solvent concentrations (20 to 40 percent), although the concentration of NMP may range from 12 to 80 percent. NMP is a larger molecule than DCM and has lower vapor pressure, lower volatility, and higher surface tension. Thus, NMP-based strippers act slower than DCM-based paint strippers. They can dissolve multiple paint layers, however, which allows less solvent to be used. NMP paint strippers have a higher safety margin for inhalation than DCM. At 20°C, the equilibrium vapor concentration of NMP is 300 ppm, compared to 450,000 ppm for DCM.[31]

NMP-based formulas are also applicable in OEM. NMP can strip acrylic latex gloss enamel, household epoxy spray paint, polyurethane gloss enamel, high gloss wood

finish, and tallow oil alkyd spray paint. The concentration of NMP in a paint stripper depends on the application and type of coating to be stripped. In the consumer market, the NMP-based paint strippers have a high concentration of NMP.[32]

EPA recently completed a study to evaluate the use of an NMP-based paint stripping formulation as a substitute for a DCM-based product. The study was conducted at Tooele Army Depot on a cleaning line designed for depainting, cleaning, and applying conversion coatings to nonferrous engine parts and powertrain subassemblies. The NMP product also contained monoethanolamine as a co-solvent. Preliminary results of the study indicate that NMP worked well, but took a little longer than DCM to strip paint. The study also found that NMP was less expensive than DCM and could be used as a drop-in replacement in existing equipment. This would allow the facility to achieve substantial savings by making the switch from DCM to NMP.[33]

EPA OPPT recently completed a study of NMP, *Life Cycle Analysis and Pollution Prevention Assessment for NMP in Paint Stripping*. The study is a detailed evaluation of consumer uses of NMP and estimates or characterizes releases, exposures, and risk from the use of NMP in paint strippers. The study also evaluates risk reduction technologies. EPA OPPT is also working with the Consumer Product Safety Commission to perform an assessment of the various chemicals used in paint stripping products.[34]

In January, 1992, EPA placed NMP into a risk management evaluation after an initial review of data received from industry revealed potential mutagenicity, developmental and reproductive toxicity effects of NMP. In April, 1992, EPA informed NMP manufacturers that it was concerned that exposure to NMP may potentially result in adverse health effects on reproduction and development. In November, 1993 EPA signed an Enforceable Consent Agreement pursuant to the Toxic Substances Control Act with ARCO, BASF, and International Specialty Products to perform

certain health effects tests with NMP. Required tests include pharmokinetics, subchronic toxicity, functional observation, motor activity, neuropathology, and oncogenicity. The deadlines for final reporting of test results range from 6 months from the effective date for the 28 day subchronic toxicity range finding study to 72 months from the effective date for oncogenicity.

Dibasic Esters. DBEs are refined dimethyl esters of adipic (dimethyl adipate), glutaric (dimethyl glutarate), and succinic acids (dimethyl succinate). Dimethyl adipate is synthesized by the esterification of adipic acid with methanol in the presence of an acid catalyst.[35] Dimethyl glutarate is produced by the esterification of methanol with glutaric acid.[36] Dimethyl succinate is made by the direct esterification of succinic acid with methyl alcohol in a benzene/sulfuric acid solution.[37]

Each of these DBEs use petroleum hydrocarbons or benzene somewhere in their chemical synthesis pathway. For example, adipic acid is made via oxidation of cyclohexane in two processing steps.[38] Cyclohexane is a petroleum product and is obtained by the distillation of petroleum, by hydrogenation of benzene, or from toluene by simultaneous dealkylation and double-bond hydrogenation.[39] Glutaric acid is manufactured by the oxidation of cyclopentanone with nitric acid.[40] Cyclopentanone is prepared by heating adipic acid.[41]

DBEs possess excellent solvent properties. They are stable, low-cost liquids with high boiling points. Their effectiveness can be enhanced by blending them with other solvents such as NMP. A base blend of 70 to 80 percent of DBE and 20 to 30 percent of NMP is capable of stripping a wide range of paints.[42] One disadvantage of this chemical is that the DBE-based paint stripper takes two or three times longer than DCM products to perform equivalent stripping. However, DBE-based paint strippers are able to remove a variety of coatings, including acrylic latex enamel, epoxy, nitrocellulose lacquer, and polyurethane

varnish.[43] DBEs provide low emissions because of their low volatility. An occupational limit of 1.5 ppm is recommended by the manufacturer.

Only limited data are available to evaluate the toxicity of DBEs. As a result, the Consumer Product Safety Commission recently sent a letter of inquiry to the National Toxicology Program regarding possible toxicity testing of DBEs.[44]

Process Modifications

Chemical paint strippers are used in OEM to strip paint from defective manufactured parts before repainting, clean overspray from paint spray booths, and clean process lines and spray guns used to deliver the paint to the spray booth. Many manufacturers are finding that simple product or process modifications can be made to eliminate or substantially reduce the amount of chemicals used in paint stripping without loss of quality or increased cost.

Product modifications involve reevaluation of the need for painting. Frequently parts are painted for aesthetic reasons alone, when there is no underlying technical criteria, such as corrosion protection. Manufacturers of automotive parts, for example, are finding that consumers are not concerned if under-the-hood parts are not painted if the only reason for painting the part is aesthetic. Eliminating the unnecessary painting step can include cost savings on materials and equipment used in both painting and paint stripping, and material handling and disposal costs. In addition to other cost savings, the elimination of the toxic chemicals used in paints and paint stripping provides improved working conditions and numerous intangible benefits such as improved consumer perception. The challenge for manufacturers who want to eliminate unnecessary painting processes can be to convince their clients that painting may not be necessary for consumer acceptance when the only reason for painting is aesthetic.

Process modifications involve reevaluating the method of delivery of paint to the substrate, taking into consideration factors such as paint

overspray and the influence of the paint delivery method on clean up requirements. Switching rom solvent-based spray paints to powder coatings is an example of a process modification to eliminate or reduce the use of chemical paint strippers. As discussed in Chapter 8, the overspray from powder coatings is easily cleaned up before the thermosetting resins have cross-linked in a curing oven. Thus, use of powder coatings can eliminate the need to use chemical paint strippers to clean overspray from paint booths or to clean process lines or spray guns used in the painting process. Some method of paint removal is needed, however, to remove cured powder coatings from hooks or other equipment used to hold parts in place as they pass through the curing oven.

Conclusions

Several media blasting methods have been developed that are safe, effective substitutes for chemical paint stripping in the industrial sector. These methods are less viable for the consumer, since they typically require expensive equipment. Of the media blasting methods described in this report, the plastic and starch-based methods appear to be gaining the most widespread acceptance. Still, selecting between these methods requires an evaluation of their environmental trade-offs.

Plastic-media blasting employs synthetic organic chemicals that may cause health and environmental effects during their production, but this method generates little potentially hazardous wastewater during the paint stripping process. Starch-based media blasting does not use toxic chemicals to strip paint, but does generate potentially hazardous wastewater. An evaluation of the life cycles of these products would be required to fully assess which product is the best environmental alternative.

The less volatile alternative chemical stripping formulations appear to offer an environmentally better choice for the consumer than DCM-based strippers, at least because there is less potential for exposure to NMP and DBE via inhalation. The toxicity of these substitutes needs to be better defined, however, to determine how safe they really are.

Many manufacturers are finding that simple product or process modifications can reduce or eliminate the need for paint stripping in industrial applications. These include switching to powder coatings to reduce paint clean-up requirements and eliminating the painting process altogether. Not only do these modifications save time and money, they can lead to increased worker satisfaction and improved consumer perception.

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