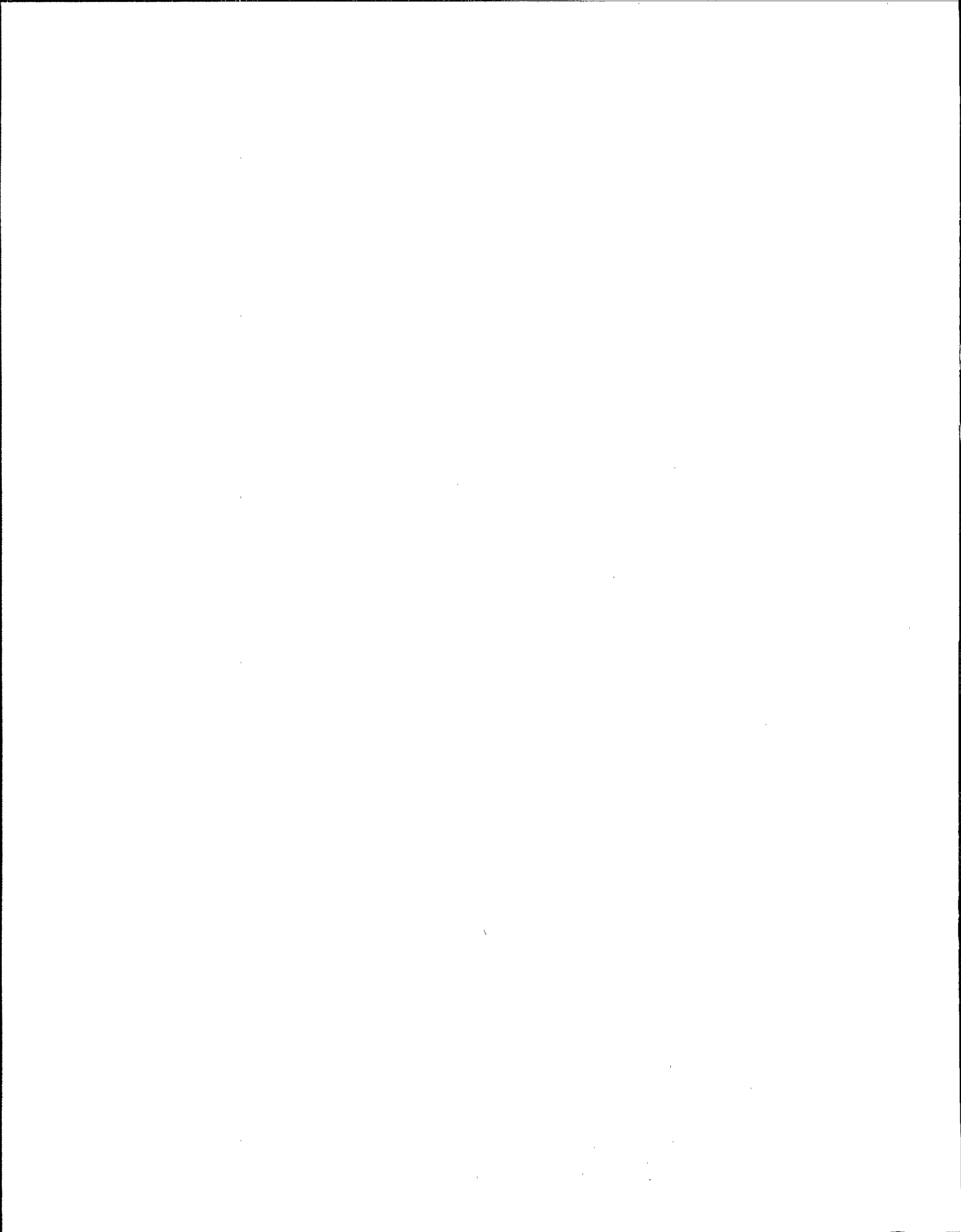




Opportunities for Pollution Prevention Research to Support the 33/50 Program





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**OPPORTUNITIES FOR POLLUTION PREVENTION RESEARCH
TO SUPPORT THE 33/50 PROGRAM**

by

**Battelle
Columbus, Ohio 43210**

**Work Assignment 06
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EPA Project Officer

**Paul M. Randall
Waste Minimization, Destruction
and Disposal Research Division**

**RISK REDUCTION ENGINEERING LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268**



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NOTICE

This review of research needs summarizes information collected from U.S. Environmental Protection Agency programs, peer reviewed journals, industry experts, vendor data, and other sources. A variety of potential candidate source reduction and recovery/recycling methods are described. This document is intended as advisory guidance in identifying research needs for reducing pollution.

Publication of this document does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use. Compliance with environmental and occupational safety and health laws is the responsibility of each individual business and is not the focus of this document.

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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 (EPA) 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 the 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 reviews common industrial uses and emerging future approaches to reducing waste of the chemical groups identified in the "33/50 Program." The Branch is charged with defining, evaluating, and advancing the technology for implementing the national pollution prevention program. It also provides technical assistance to other sections of the Agency for the purpose of reducing or eliminating pollution hazards.

E. Timothy Oppelt, Director
Risk Reduction Engineering Laboratory

ABSTRACT

The intent of this effort was to provide guidance information for the Pollution Prevention Research Branch in planning its research program. This document compiles information on existing pollution prevention methods and identifies research needs. It helps define areas for research to increase application of existing methods and create new approaches for source reduction and recovery/recycling of the 17 chemical groups targeted in the 33/50 Program. The emphasis is on source reduction, but recovery/recycling methods are also considered.

A functional approach is used to identify and organize research areas for each of the 17 targeted chemical groups. The sources and production characteristics and rates are briefly summarized. Then pollution prevention opportunities and supporting research needs are discussed for the major industrial and consumer applications of the targeted chemical groups. The opportunities and research needs are presented in both narrative and tabular formats.

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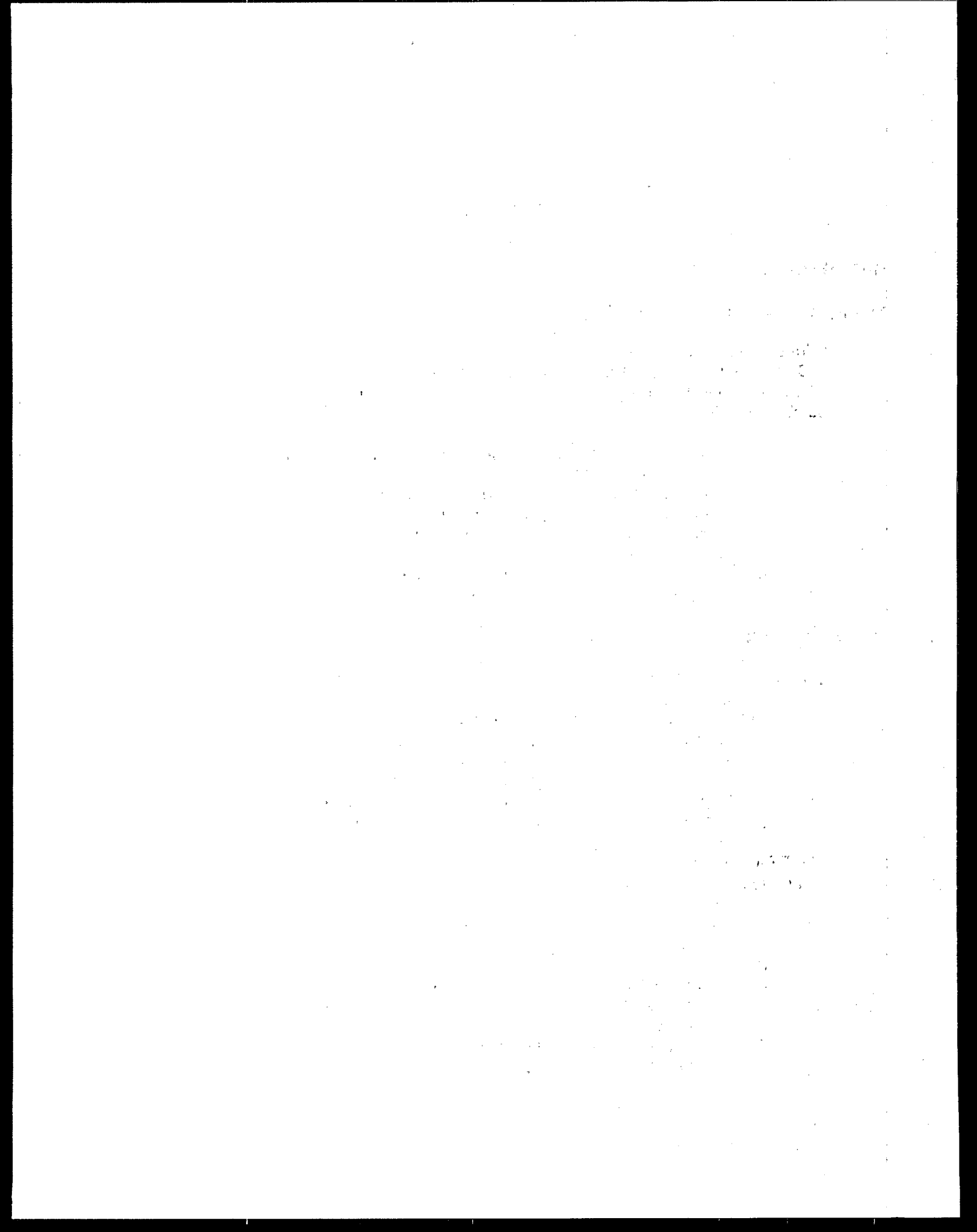
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1 INTRODUCTION

BACKGROUND

Pollution Prevention Act of 1990

Prior to passage of the Pollution Prevention Act of 1990 (PPA) in November 1990, U.S. environmental protection regulations generally focused on treatment and disposal of polluting materials rather than reduction at the source. The PPA established prevention of pollution at the source as a national policy.

1. Industry is encouraged to prevent or reduce pollution at the source wherever feasible.
2. Unpreventable pollution should be recycled in an environmentally safe manner when feasible.
3. When pollutants cannot be prevented or recycled, they should be treated.
4. As a last resort, pollutants would be disposed of or otherwise released into the environment.

Source Reduction

Source reduction, as defined by the Act, means any practice that

"reduces the amount of any hazardous substance, pollutant or contaminant entering any waste stream or otherwise released into the environment (including fugitive emissions) prior to recycling, treatment or disposal; and which reduces the hazards to public health and the environment associated with the release of such substances, pollutants, or contaminants." (U.S. EPA, 1991a)

The EPA is empowered by the PPA to establish a program for the EPA to promote source reduction. According to the PPA, the EPA will:

1. Facilitate adoption of source reduction techniques by businesses and other federal agencies.
2. Establish standard methods for measuring source reduction.
3. Determine effect of regulations on source reduction.
4. Find opportunities to use federal procurement to encourage source reduction.
5. Improve public access to data collected under federal environmental statutes.

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6. Implement a training program on source reduction opportunities, model source reduction auditing procedures, a source reduction clearinghouse, and an annual award program.

What Is the 33/50 Program?

The 33/50 Program is EPA's voluntary pollution prevention initiative to reduce national pollution releases and off-site transfers of 17 toxic chemicals by 33% by the end of 1992 and by 50% by the end of 1995. EPA is asking companies to examine their own industrial processes to identify and implement cost-effective pollution prevention practices for these chemicals. Company participation in the 33/50 Program is completely voluntary. The Program aims, through voluntary pollution prevention activities, to reduce releases and off-site transfers of a targeted set of 17 chemicals from a national total of 1.4 billion pounds in 1988 to 700 million pounds by 1995, a 50% overall reduction. The Toxics Release Inventory (TRI) (established by federal law, the Emergency Planning and Community Right-to-Know Act of 1986) will be used to track these reductions using 1988 data as a baseline. As required by the Pollution Prevention Act of 1990, TRI industrial reporting requirements were to be expanded, beginning in calendar year 1991, to include information on pollution prevention.

EPA announced the 33/50 Program in February 1991 when EPA Administrator William K. Reilly asked 600 U.S. companies to reduce their releases of these 17 toxic chemicals. EPA contacted these 600 companies first because TRI data indicated that these companies were the largest dischargers to the environment of these chemicals. EPA is also contacting thousands of additional companies that release these 17 chemicals and requesting their voluntary participation in the 33/50 Program. All companies are encouraged to participate in the 33/50 Program (even if they do not receive a letter from EPA inviting them to participate).

While EPA is seeking to reduce aggregate national environmental releases of these 17 chemicals by 50% by 1995, individual companies are encouraged to develop their own reduction goals to contribute to this national effort. EPA also encourages companies to reduce releases of other TRI chemicals and to extend these reductions to their facilities outside the United States. For those companies that have not yet made a commitment to participate, EPA encourages them to participate in this national pollution prevention initiative. EPA will periodically recognize those companies that commit to reduce their releases and transfers of the targeted chemicals, and will publicly recognize the pollution prevention success companies achieve. (U.S. EPA, 1991b; U.S. EPA, 1992)

What Is Pollution Prevention?

The overall goal of the 33/50 Program is to promote the benefits of pollution prevention while obtaining measurable reductions in pollution. Pollution prevention

is the use of materials, processes, or practices that reduce or eliminate the creation of pollutants or wastes.

Pollution prevention should be considered the first step in a hierarchy of options for reducing the generation of pollution. The next step in the hierarchy is responsible recycling of any wastes that cannot be reduced or eliminated at the source. Wastes that cannot be recycled should be treated in accordance with environmental standards. Finally, any wastes that remain after treatment should be disposed of safely.

EPA is promoting pollution prevention because it is often the most cost-effective option to reduce pollution, and the environmental and health risks associated with pollution. Pollution prevention is often cost effective because it may reduce raw material losses; reduce reliance on expensive "end-of-pipe" treatment technologies and disposal practices; conserve energy, water, chemicals, and other inputs; and reduce the potential liability associated with waste generation. Pollution prevention is environmentally desirable for these very same reasons: pollution itself is reduced at the source while resources are conserved.

Major 33/50 Program Goals

The 33/50 Program has three basic goals. First, EPA is aiming to reduce national aggregate environmental releases of the 17 target chemicals from 1988 levels by 33% by the end of 1992 and by 50% by the end of 1995. Second, EPA is encouraging companies to use pollution prevention practices (rather than end-of-pipe treatment) to achieve these reductions. Third, EPA hopes that this Program will help **foster a pollution prevention ethic** in American business whereby companies routinely analyze all their operations to reduce or eliminate pollution before it is created.

What Are the Target Chemicals?

The 17 chemical groups are:

Benzene	Methyl Ethyl Ketone
Cadmium & Cadmium Compounds	Methyl Isobutyl Ketone
Carbon Tetrachloride	Nickel & Nickel Compounds
Chloroform	Tetrachloroethylene
Chromium & Chromium Compounds	Toluene
Cyanide & Cyanide Compounds	1,1,1-Trichloroethane
Lead & Lead Compounds	Trichloroethylene
Mercury & Mercury Compounds	Xylenes
Methylene Chloride	

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These chemicals were selected from the Toxics Release Inventory (TRI). The TRI is a computerized database containing public information on the annual releases and transfers of approximately 300 toxic chemicals reported by U.S. manufacturing facilities to EPA and the States. Since 1987 federal law has required facilities to report the amount of both routine and accidental releases of the 300 listed chemicals to the air, water, and soil, and the amount contained in wastes transferred off-site.

The chemicals listed above were selected for the 33/50 Program because:

1. They are produced in large quantities and subsequently released into the environment in large quantities.
2. They are generally identified as toxic or hazardous pollutants; thus there may be significant environmental and health benefits from reducing their releases to the environment.
3. There is the potential to reduce releases of these chemicals through pollution prevention.

The 33/50 Program Signals a New Approach

The 33/50 Program complements EPA's traditional command and control approach. The key attributes of this new approach are:

National in Scope. Success will be measured according to whether reductions have been achieved nationwide, rather than for each company or facility. The reductions also will be looked at as an aggregate — total releases of all chemicals rather than for each one.

Voluntary. Companies are free to decide if and how to participate in the program by: a) committing to meet their own specified reduction goals; and b) making good faith voluntary efforts to identify and implement cost-effective prevention measures. Any steps taken to reduce targeted toxics will not be enforceable, unless these activities are otherwise required by law or regulation.

Multi-Media. The reduction goals apply to total releases and off-site transfers to air, land, and water.

Prevention-Oriented. EPA's objective is to encourage these reductions through pollution prevention. However, companies are encouraged to participate in the 33/50 Program even if all of their reductions are not achieved through prevention.

What Is EPA Asking Companies to Do?

EPA is contacting thousands of companies to provide them with information on the 33/50 Program and to solicit their participation. Each company is being asked to examine its processes to identify and implement cost-effective pollution prevention

practices that will reduce or eliminate releases of the 17 chemicals. In addition, companies are being asked to submit a letter to EPA publicly stating their reduction goals and how they plan to achieve them. All companies wishing to participate in the 33/50 Program and receive official public recognition of their commitments are encouraged to supply EPA with information on their reduction goals.

How to Get More Information

Guidance on how a company can participate in the 33/50 Program is available upon request. For copies of this commitment guidance and other 33/50 Program documents, fax your request to the TSCA Assistance Service at (202) 554-5603. For more information on the 33/50 Program, contact the TSCA Hotline at (202) 554-1404, (8:30 am to 4:00 pm).

Information on pollution prevention (and the 33/50 Program) is available through the Pollution Prevention Information Exchange System (PIES), a free computer bulletin board associated with EPA's Pollution Prevention Information Clearinghouse. To learn how to use the Clearinghouse and the PIES, call (703) 821-4800. To access the PIES using a PC, a modem, and communications software, call (703) 506-1025 (set your communications software to no parity, 8 data bits, and 1 stop bit).

Toxic Release Inventory Database

The computerized Toxic Release Inventory (TRI) database was established to track toxic releases by the Emergency Planning and Community Right-to-Know Act of 1986. The TRI contains public information on the annual releases and transfers of approximately 300 toxic chemical groups. U.S. manufacturing facilities report on these chemical groups to the EPA and the states. The law requires reporting of both routine and accidental releases of these 300 chemical groups to the air, water, and soil, and the amount contained in wastes transferred to off-site locations. The TRI includes the 17 chemical groups selected for the 33/50 Program based on these reasons:

1. They are produced, and subsequently released, in large quantities. Collectively, more than 6,000 parent companies reported 1.4 billion pounds of releases or off-site transfers of these 17 chemical groups in 1988.
2. Because they are generally identified as toxic or hazardous pollutants, significant environmental and health benefits may accrue from reducing their releases to the environment.
3. Their releases potentially may be reduced through pollution prevention.

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The PPA requires facilities that report releases for the TRI to report on pollution prevention and recycling. Information would include quantity entering the waste stream, percentage change from the previous year, source reduction practices, and changes in production from the previous year.

The 17 priority chemical groups are listed in Table 1. The chemicals are chiefly heavy metals, chlorinated organic compounds, and nonchlorinated solvents. These high-priority chemicals are of the greatest concern to the EPA's air, water, land, and toxic chemical control programs. The EPA sought a way to reduce their serious known health and environmental effects and to limit their exposure.

To help focus the discussion of pollution prevention research needs for the 17 chemical groups, releases and transfers reported in the 1988 TRI data are summarized in Tables 2 and 3. Table 2 shows the reported releases for each chemical by release/transfer path. Table 3 details releases and transfers by industry. The 50 industries, identified by the four-digit Standard Industrial Category (SIC), for each chemical are grouped by two-digit SIC. All other four-digit SICs are grouped as others.

OBJECTIVE

This document compiles information on existing and emerging source reduction and recovery/recycling methods for each of the 17 priority chemicals targeted in the 33/50 Program. It provides an overview of many common uses of the priority chemicals and potential methods for reducing waste of the chemicals. Based on these uses and waste reduction methods, research needs are identified. The research needs describe functional requirements for research to expand the application of existing methods or to foster rapid development of emerging methods.

This document provides a preliminary review of a broad range of candidate methods. It is intended to focus development and screening of new ideas and to facilitate planning for research projects in source reduction and recovery/recycling. Selection of research opportunities is concerned with the efficient allocation of money, skills, equipment, and facilities to projects. Careful selection of projects is essential to efficient use of limited resources. Research efforts should be focused on projects that give a significant reduction of the target chemicals and have a reasonable probability of success.

TABLE 1. PROPERTIES OF THE TRI TARGET CHEMICALS

Compound	Formula	Molecular Weight	Density mg/l (at °C)	Melting Point °C	Boiling Point °C	Vapor Pressure mm Hg (at °C)	Solubility in Water mg/l (at °C)
Benzene	C ₆ H ₆	78.11	0.88(20)	5.5	80.1	76(20)	1,800(20)
Cadmium	Cd	40.08	8.65(20)	320.9	767	nil	i
Carbon Tetrachloride (Tetrachloromethane)	CCl ₄	153.82	1.59(20)	-23	76.7	113(25)	800(25)
Chloroform (Trichloromethane)	CHCl ₃	119.38	1.49(20)	-64	62	160(20)	9,300(25)
Chromium	Cr	52.01	7.14	1615	2200	nil	i
Cyanide	CN ⁻	13	N/A	N/A	N/A	N/A	N/A
Dichloromethane (Methylene Chloride)	CH ₂ Cl ₂	84.93	13.3(20)	-97	41	349(20)	20,000(20)
Lead	Pb	207.21	11.3	327.5	1620	nil	i
Mercury	Hg	200.61	13.5	-38.87	356.9	low	i
Methyl Ethyl Ketone (2-Butanone)	CH ₃ COCH ₂ CH ₃	72.1	0.80(20)	-86.4	79.6	77.5(20)	260,000(25)
Methyl Isobutyl Ketone (4-Methyl-2-pentanone)	(CH ₃) ₂ CHCH ₂ COCH ₃	100.2	0.80(20)	-83	118	6(20)	17,500(25)
Nickel	Ni	58.69	8.9	1452	2900	nil	i
Tetrachloroethylene (Perchloroethylene)	CCl ₂ =CCl ₂	165.83	1.63(20)	-22.7	121.4	14(20)	150(25)

TABLE 1. PROPERTIES OF THE TRI TARGET CHEMICALS (Continued)

Compound	Formula	Molecular Weight	Density mg/l (at °C)	Melting Point °C	Boiling Point °C	Vapor Pressure mm Hg (at °C)	Solubility in Water mg/l (at °C)
Toluene (Methylbenzene)	$C_6H_5CH_3$	92.1	0.87(20)	-95.1	110.8	22(20)	640(25)
1,1,1-Trichloroethane (Methylchloroform)	CCl_3CH_3	133.41	1.35(20)	-32	71 to 81	100(20)	4,400(20)
Trichloroethylene (Ethylene trichloride)	$CCl_2=CHCl$	131.5	1.46(20)	-87	86.7	60(20)	1.1(25)
p-Xylene	$C_6H_4(CH_3)_2$	106.17	0.86(20)	13	138.4	6.5(20)	198(25)
m-Xylene	$C_6H_4(CH_3)_2$	106.17	0.864(20)	-48/-53	139	6(20)	ND
o-Xylene (Dimethylbenzene)	$C_6H_4(CH_3)_2$	106.17	0.88	-25	144.4	5(20)	175(20)

ND = No data

N/A = Not applicable

i = insoluble

Sources: Perry and Chilton (1963)
Verschuere (1983)

TABLE 2. REPORTED RELEASES IN 1988 FOR EACH CHEMICAL BY
RELEASE/TRANSFER PATH (IN 1,000 POUNDS)^(a)

Compound	Total Air	Water	Underground Injection	Land Disposal	POTW Transfer	Other Transfer	Grand Total
Benzene	28,118	47	636	221	1,102	2,973	33,097
Cadmium	119	4	2	542	20	1,361	2,049
Carbon Tetrachloride	3,683	16	98	15	5	1,187	5,003
Chloroform	22,974	1,089	36	68	1,227	1,468	26,862
Chromium	1,181	389	101	28,125	2,108	24,961	56,866
Cyanide	1,981	193	7,461	106	1,148	2,916	13,806
Lead	2,588	237	3	27,494	208	28,178	58,707
Mercury	26	1	0	14	2	275	318
Methylene Chloride	126,796	347	665	157	2,584	22,085	153,435
Methyl Ethyl Ketone	127,676	77	214	155	933	30,003	159,057
Methyl Isobutyl Ketone	30,524	762	122	32	1,509	10,761	43,709
Nickel	540	210	153	3,644	882	14,001	19,429
Toluene	273,753	254	1,432	883	3,544	64,762	349,628
Tetrachloroethylene	32,277	33	72	106	586	4,428	37,503
1,1,1-Trichloroethane	170,421	94	1	187	293	19,481	190,477
Trichloroethylene	49,071	14	0	21	71	6,231	55,416
Xylene	155,889	299	123	834	4,214	40,215	201,574
Subtotal	1,027,618	4,068	11,120	62,604	20,442	276,085	1,401,936

^(a)Based on 1988 Toxic Release Inventory Reports

TABLE 3. RELEASES AND TRANSFERS IN 1988 OF THE TRI CHEMICALS BY INDUSTRY (IN 1,000 POUNDS)^(a)

SIC ^(b)	Benzene	Cadmium	Carbon Tetra- chloride	Chloroform	Chromium	Cyanide	Lead	Mercury	Methylene Chloride	Methyl Ethyl Ketone	Methyl Isobutyl Ketone	Nickel	Toluene	Tetra- chloro- ethylene	1,1,1- trichloro- ethane	Trichloro- ethylene	Xylene
20	2			39					5,451	1,310		488					
22		2					87		11,346	1,657			11,061	684	1,044	895	1,760
23														187			
24	5			714	181					2,104	1,056		4,955				7,759
25						2			1,232	4,603	1,964	69	15,449		891		9,883
26	6			21,686	126			18	414	9,079	860		50,596		2,529		2,063
27										3,852	984		44,868	584	2,326		
28	12,697	453	4,840	4,333	9,913	10,245	2,571	238	46,936	16,625	16,787	2,814	72,087	3,024	2,151	915	44,760
29	6,482	2	29		1,114	4	459	1		6,874	794	841	16,300				11,208
30	1	29	1			91	546		29,512	21,115	2,280	191	26,791	916	13,627	2,139	6,288
31		2			1,800		112			2,120	1,171		1,523				916
32	23	0	0	0	1,404		3,264	0	1,694	934	133	295	1,998			1,343	
33	12,962	540			27,688	2,131	42,057		548	5,210	2,094	6,555	5,269	2,730	15,458	3,466	6,277
34	0	749	132		4,359	954	2,677		4,995	10,803	2,323	3,832	3,336	3,943	21,916	11,728	13,524
35	63	4			2,886	7			1,543	2,073	182	736		3,884	7,564	5,959	5,662
36		214		2	150	106	3,731	61	10,453	13,215	149	983	7,682	3,903	15,965	5,195	10,822
37	376	48		68	3,485	234	1,702		8,533	17,713	6,150	1,012	14,976	9,389	32,693	10,428	42,312
38			0	6			61		22,942	1,998	454	67	3,453	450	2,592	1,190	
39	1	1			228	6			2,026	4,113	534	322	3,207	454	3,934	573	
Others	481	0		13	3,552	27	1,439		17,156	23,953	4,137	1,224	61,076	7,355	67,786	11,587	38,445
Subtotal	33,097	2,049	5,003	26,862	56,866	13,806	58,707	318	153,435	159,057	43,709	19,429	344,628	37,503	190,477	55,416	201,574
Total	1,401,936																

^(a)Based on 1988 Toxic Release Inventory Reports

^(b)SIC listing based on the 50 four-digit SIC industries with the largest reported total release

POTENTIAL USERS OF THIS DOCUMENT

This document broadly scopes the functional requirements of research needed to develop source reduction methods for the priority chemicals. The document is intended for those in charge of 33/50 Program application, for R&D and process development personnel at companies where releases or off-site transfers of the 17 priority chemical groups take place, and for researchers and process development personnel at other companies doing independent research on source reduction technologies, and on recovery and recycling operations.

The purpose of this document is to present interesting and stimulating challenges leading to new ideas for research in the development of new methods for source reduction and recovery/recycling.

Although examples are used to clarify the discussion, the definition of research needs describes the functions needed without reference to a specific approach. Specifications of the research needs are, as much as possible, stated as functions to avoid limiting creativity in developing new ideas. There is also an attempt to make the statement of research needs sufficiently general to ensure the resulting technologies have wide application and to avoid projects requiring a large component of proprietary intellectual property.

REFERENCES FOR THE INTRODUCTION

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2 CADMIUM POLLUTION PREVENTION RESEARCH NEEDS FOR THE 33/50 PROGRAM

SOURCES AND PRODUCTION CHARACTERISTICS AND RATES

Cadmium (chemical symbol Cd) is a Group II-B element in the Periodic Table and exhibits a +II oxidation state in almost all of its compounds. Pure cadmium compounds are rarely found in nature, although occurrences of greenockite, CdS, and otavite, CdCO₃, are known. The main sources of cadmium are sulfide ores of lead, zinc, and copper, from which cadmium is recovered as a by-product of production of these ores. Because cadmium is produced as a by-product of sulfide ore refining, reducing cadmium consumption may not directly affect cadmium production rates. However, reducing cadmium use will avoid distribution of cadmium throughout the environment and should, therefore, be pursued.

Cadmium is obtained in vapor form when roasting sulfide ores, and as a sludge from zinc sulfate purification. Pure cadmium metal is silver-white, tinged with blue, and lustrous. Cadmium is often converted to its oxide, CdO, where it is a more convenient starting material for synthesis of other compounds.

Of the estimated 4,080 tons of cadmium consumption in 1990, the U.S. Bureau of Mines (1991) has approximated apparent consumption patterns as follows:

batteries	40%
coating and plating	25%
pigments	13%
plastics and synthetic products	12%
alloys and other uses	10%

Cadmium and its compounds are highly toxic. Most poisoning cases have been reported to be due from inhalation of fumes or dusts. Fumes are formed at high temperatures by such industrial processes as welding and brazing, and they may be released from incinerators that are unequipped with pollution control devices. Cadmium is immediately dangerous to human health upon exposure to 1 mg/m³ over an 8-h period (Chizikov, 1966) and is lethal in air concentrations of 6 mg/m³ over an 8-h period (Barrett and Card, 1947). Cadmium causes a range of systemic effects, for example, kidney and lung damage. Some shellfish tend to concentrate cadmium and it causes chronic effects in many aquatic organisms.

A variety of cadmium applications and potential approaches for reducing waste are summarized in Table 4 and are outlined in the text following the table.

TABLE 4. CADMIUM POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Electrical applications	Replace cadmium hydroxide in Ag-Cd and Ni-Cd batteries	Determine the performance requirements for rechargeable and high-performance batteries. Identify test methods for performance measurement. Test the alternative candidates.
	Eliminate cyanide pollution from cadmium plating	Test and evaluate the characteristics of cadmium plating without the use of cyanide.
	Use alternatives to cadmium plating — use ion vapor deposition (IVD) aluminum	
Pigments	Use nonhazardous materials for pigment	Verify the use of IVD aluminum as a replacement for cadmium in commercial applications. Find alternative nonhazardous substances — determine the performance requirements for cadmium pigments
	Minimize the use of cadmium pigments	Find methods of improving performance without adding more pigment.
	Use components other than cadmium compounds for stabilizers	Search for nonhazardous materials that can prevent PVC and other polymers from discoloring.
Alloys	Use a non-cadmium alloy with silver	Examine the properties of pure metals and alloys
	Use a plastic or composite alternative	Examine the properties of plastics and composites

TABLE 4. CADMIUM POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Alloys (continued)	Optimize traditional alloying operations	Improve traditional processing operations
	Recover or recycle cadmium in alloying process	Improve the performance of separation technology. — use ion-specific techniques
	Change synthesis path to avoid the need of a cadmium catalyst or use a nonhazardous catalyst	Determine the requirements for specific reaction pathways — identify test methods to measure the purity, yield, and other requirements of the syntheses product — identify possible alternative reaction pathways
Other uses	Eliminate cadmium from miscellaneous uses	Identify and test nonhazardous catalysts as alternatives for cadmium-compound catalysts.
		Research is needed to fully understand the role of cadmium in these various uses — find viable alternatives.

POLLUTION PREVENTION OPPORTUNITIES AND SUPPORTING RESEARCH NEEDS

Electrical Applications

Cadmium hydroxide is used as the active anode material in rechargeable silver-cadmium and nickel-cadmium batteries. Silver-cadmium oxide material is used to make electrical contacts, cadmium chalcogenide electroluminescent and photoconductive devices, as well as phosphors and several types of semiconductors. Cadmium arsenides, antimonides, and phosphides are used in many electronic devices and semiconductors. A minor use of cadmium sulfide is in the manufacture of photovoltaic solar cells.

Replace cadmium hydroxide in Ag-Cd and Ni-Cd batteries. Alternative materials may be available for battery anodes.

Research needs. Research is needed to determine the performance requirements for rechargeable and high-performance batteries and to identify test methods to measure performance with respect to those standards. Then candidate materials can be identified and tested as alternatives.

Coating and Plating

Cadmium is used in plating because it has properties that are superior to those of other coatings for some applications. It is used to plate fasteners to help ensure that the parts pass *torque-tolerance* tests, which simulate the action of a power wrench tightening a nut on a bolt. The nut should tighten quickly under the proper applied torque and hold securely thereafter. Cadmium is a soft metal and has natural lubricity, which give it good torque properties. It also has good corrosion resistance and meets salt-spray tests used in the automotive industry. In the past, numerous military specifications have required the use of cadmium.

The major cadmium complex used in electroplating is cadmium cyanide, $\text{Cd}(\text{CN})_4^{-2}$; other plating salts include cadmium sulfate, sulfamate, chloride, fluoroborate, and pyrophosphate. Cadmium borates are used with a fluoroborate process for electrodeposition of cadmium in high-strength steels. Cadmium oxide is used in electroplating baths, dissolved in excess sodium cyanide. Cadmium sulfate is used in electrodeposition of cadmium.

Eliminate cyanide pollution from cadmium plating. Traditionally, most cadmium plating is done using cyanide because of its excellent throwing power. Other plating solutions are being tried that do not contain cyanide and offer high cathode efficiency at high current

Research needs. Research is needed to test and evaluate the characteristics of cadmium plating performed without cyanide.

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density. These baths contain metallic salts such as neutral sulfates, acid sulfates, and acid fluoroborates. Non-cyanide baths are often preferred for cadmium plating of quenched and tempered high strength steels because less hydrogen is generated, thus lessening the danger of embrittlement. Ajax Metal Processing in Detroit plates a large number of parts using a proprietary non-cyanide method.

Use an alternative to cadmium plating, such as ion vapor deposition (IVD) aluminum. IVD aluminum has recently been used as a substitute for cadmium plating in aircraft parts because of its excellent corrosion resistance and because it meets or exceeds most of cadmium's performance features (Holmes et al., 1989; Rizzi et al., 1986).

Research needs. Research is needed to verify that IVD aluminum can be used in place of cadmium plating for commercial applications.

Pigments

Cadmium sulfide, cadmium sulfo-selenide, and lithopone pigments are used to produce a range of colors, including yellow, orange, red, and maroon. These colorants are sometimes used in plastics, paints, rubber, paper, glass, inks, and ceramic glazes, although pigment applications are being reduced.

Use nonhazardous materials for pigment. Alternative nonhazardous materials may be available for coloration.

Research needs. Research is needed to determine the performance requirements for cadmium pigments and to find alternative substances that are nonhazardous.

Minimize use of cadmium pigments. It may be possible to reduce the amount of cadmium compounds used on a coating material.

Research needs. Research is needed to determine the performance requirements for cadmium pigments and to find methods of improving performance without adding more cadmium pigment.

Plastics and Synthetic Products

Organocadmium salts are used as heat and light stabilizers in some plastics, particularly PVC, to retard discoloration. Cadmium salts of organic acids are used together with barium soaps to produce stabilizers for plastics.

um in stabilizers would account for a large savings in cadmium usage.

that can be substituted for cadmium compounds to prevent PVC and other polymers from discoloring.

Alloys

Cadmium oxide is used in the manufacture of silver alloys.

Use a non-silver alloy. Non-silver alloys may be used to fabricate products that do not specifically require silver's physical properties to perform their functions.

Research needs. Research is needed to examine the properties of pure metals and alloys in order to determine if they may be adapted for use in place of silver-alloys.

Use a plastic or composite alternative. Products that do not require silver's electrical or physical properties to perform their functions may be fabricated instead from plastic or composite materials. Substitutions of this sort may be possible in low-temperature applications, such as decorative cast materials.

Research needs. Research is needed to examine the properties of plastics and composites in order to determine if they may be adapted for use in place of silver-alloys.

Optimize traditional alloying operations. If cadmium cannot be avoided, improvements can be developed to reduce waste in traditional operations.

Research needs. Areas of need may exist to decrease waste and improve recycling in traditional processing operations.

Recover or recycle cadmium in alloying process. Develop methods to remove impurities in cadmium-alloys used for casting, plating, or other processes, to extend lifetime of the melt. For example, ion-specific separation methods may be needed to allow reprocessing.

Research needs. Research is needed to improve the performance of separation technology. Ion-specific techniques may be used in this regard.

Catalysts

Cadmium dialkyls and many inorganic cadmium salts are used as catalysts, particularly for organic polymerization reactions. Cadmium carbonate is used as a catalyst in the production of other cadmium compounds. Cadmium tungstate is an industrial catalyst.

Change synthesis path to avoid the need of a catalyst or use a nonhazardous catalyst. Different combinations of chemical feedstocks

Research needs. Research is needed to determine the requirements for specific reactions and to identify test methods to measure the purity, yield, and other requirements. Then

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Different combinations of chemical feedstocks may allow preparations of the desired product without the need for a catalyst.

tions and to identify test methods to measure the purity, yield, and other requirements. Then candidate reaction paths can be identified and tested as alternatives for paths requiring cadmium compounds as catalysts.

Other Uses

Cadmium chloride is used in photography, dyeing and cloth printing, special mirrors, and lubricants. Cadmium nitrate is used in photographic emulsions.

Eliminate cadmium from miscellaneous uses. Find alternative materials with similar performance features as cadmium for substitution into product or process.

Research needs. Research is needed to fully understand the role of cadmium in these various uses in order to find viable alternatives.

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3 CHROMIUM AND NICKEL POLLUTION PREVENTION RESEARCH NEEDS FOR THE 33/50 PROGRAM

SOURCES AND PRODUCTION CHARACTERISTICS AND RATES

Chromium is a naturally occurring hard, brittle, steel-gray metal. It is produced from chromite ores. Chromium has a wide range of uses in three primary consumption groups. The metal is a major constituent in stainless steel and other specialty ferrous and nonferrous alloys. Of the 418,924 tons of chromium ferroalloys, metal, and other chromium-containing metals used in 1988, stainless steel accounted for 80% of the reported consumption. Manufacture of refractory bricks to line metallurgical furnaces used 88,750 tons of chromite in 1988. The chemical industry consumed chromite for manufacturing sodium bichromate, chromic acid, and pigments (BOM Cr, 1988). Chromium chemicals, such as chromic acid, are frequently used in metal plating applications.

Nickel is a naturally occurring malleable, silvery metal. Nickel ores occur mainly as sulfides or oxides, with sulfides accounting for about two-thirds of the world's supply. The reported consumption of nickel in 1988 was 195,758 tons. Nickel, like chromium, is a major constituent of austenitic stainless steels. Stainless steel accounted for 40% of the reported nickel consumption in 1988. Nonferrous and superalloys accounted for another 31% of nickel consumption. Electroplating was the next largest nickel use at 17% (BOM Ni, 1988). Nickel is also used as a catalyst and in batteries, pigments, and specialty ceramics.

A variety of chromium and nickel applications and potential approaches for reducing waste are summarized in Table 5 and are outlined in the text following the table.

TABLE 5. CHROMIUM AND NICKEL POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Plating for hardness and corrosion resistance	Use an alternative substrate that does not need chromium or nickel plating	<ul style="list-style-type: none"> Identify and validate alternative substrate Define performance requirements Develop performance testing methods Identify alternative materials Test alternative materials
	Use nonaqueous plating for chromium or nickel pollution prevention (Gresham, 1991)	<ul style="list-style-type: none"> Identify and validate new coating methods Define performance requirements <ul style="list-style-type: none"> hardness (e.g., ASTM E 384) adhesion surface roughness coating lubricity maximum coating thickness fatigue life maximum allowed temperature internal stress in coating coating corrosion resistance Determine process controls <ul style="list-style-type: none"> deposition conditions surface cleaning stripping and rework methods coating behavior on complex shapes
	Plate with a less hazardous metal (Groshart, 1989; Schiffelbein, 1991)	<ul style="list-style-type: none"> Identify and validate new aqueous plating methods Define performance requirements <ul style="list-style-type: none"> same as nonaqueous as well as hydrogen embrittlement Determine process controls <ul style="list-style-type: none"> bath conditions surface cleaning stripping and rework methods coating behavior on complex shapes

TABLE 5. CHROMIUM AND NICKEL POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Plating for hardness and corrosion resistance (continued)	Replace hexavalent chromium with trivalent chromium plating (PsF, 1988)	<p>Optimize plating with trivalent chromium</p> <ul style="list-style-type: none"> — Increase thickness and hardness of trivalent plating to allow its use for hard chromium plating — Develop method to provide "blue" color of hexavalent chromium plating rather than "gray" color of trivalent chromium plating — Develop additives to minimize the effect of higher cost of trivalent chromium plating baths — Refine operating practices to minimize the effect of higher cost of trivalent chromium plating baths — Develop smaller electrode shields for use in trivalent chromium plating tanks
	Optimize traditional plating operations (PsF, 1988)	<p>Optimize plating and rinsing</p> <ul style="list-style-type: none"> — Determine conductivity specifications for optimum rinsing bath operations — Quantify viscosity/temperature effects to allow optimization of bath temperatures — Quantify mixing effects to allow optimization of plating tank agitation
	Recover or recycle plating and rinse baths (Walker et al., 1990)	<p>Optimize reuse and recycle</p> <ul style="list-style-type: none"> — Improve performance of evaporation, reverse osmosis, or ion exchange in solutions with high salt concentration or low pH — Develop chromium or nickel selective ion exchange, crown ethers, membranes, or other separation methods
Plating for appearance	Use a non-chromium or non-nickel appearance coating (e.g., refractive plastic or other coatings)	<p>Identify and validate alternative coating</p> <ul style="list-style-type: none"> — Determine performance requirements — Develop testing methods — Identify alternative coating — Test new coating material

TABLE 5. CHROMIUM AND NICKEL POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Plating for appearance (continued)	As above in plating for hardness or corrosion resistance, use different substrate, different metal coating, optimize plating operation, and/or optimize recycling	
Surface etching, preparation, and cleaning	Use alternative etchant for silicon wafer testing (Dickens and Cannon, 1991)	Identify and validate alternative silicon wafer etching solution <ul style="list-style-type: none"> — Provide adequate etching speed — Meet or exceed current flaw detection requirements — Provide compatibility with final use of silicon wafer
	Use alternative oxidizing to prepare metal surfaces for coating or other use (Bibber, 1991; Carrillo et al., 1991; Stewart, 1991)	Identify and validate alternative anodizing solution <ul style="list-style-type: none"> — Provide corrosion resistance (e.g., ASTM B 177) — Provide adequate paint adhesion — Provide adequate impact resistance — Provide adequate anodic coating (e.g., ASTM B 137)
Alloying	Use non-chromium, non-nickel alloy, or non-metal to replace Stellite™, stainless steel, chromium steel, or other alloys	Identify and validate alternative alloys <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative alloys — Test alternative alloys
	Increase recycle of high performance alloys	Identify and validate recycle options <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative recycle options — Test alternative recycle options
Water treatment chemicals	Expand use of non-chromium treatment chemicals	Identify and validate alternative water treatment chemicals <ul style="list-style-type: none"> — Develop additives to protect multi-metal (Cu, Al, and Fe) cooling systems under wide range of pH and Eh conditions and high heat flux

TABLE 5. CHROMIUM AND NICKEL POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Refractories	Use non-chromium refractories	Identify and validate alternative refractory materials <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative refractories — Test alternative refractories
Catalysts	Change synthesis path to avoid need for catalyst	Identify and validate alternative reaction paths <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify new reaction paths — Test new reaction paths
	Optimize system to reduce catalyst use (Licis et al., 1991; Nelson, 1990)	Improve operating efficiency <ul style="list-style-type: none"> — Determine reaction kinetics — Develop improved measurement and control systems
	Improve reaction yield with the catalyst (Licis et al., 1991; Nelson, 1990)	Identify and validate improved catalyst support matrix <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative support matrix — Test alternative support matrix
		Identify and validate methods to improve catalyst selectivity <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative catalysts — Test alternative catalysts
	Use nonhazardous catalyst	Identify and validate alternative catalysts <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative catalysts — Test alternative catalysts

TABLE 5. CHROMIUM AND NICKEL POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Catalysts (continued)	Recycle catalysts (Licis et al., 1991; Nelson, 1990)	Identify and validate catalyst recycle systems <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative catalyst recycle systems — Test alternative catalyst recycle systems
Wood treatment and preserving	Replace chromated copper arsenate as chemical treatment for wood preserving (Licis et al., 1991)	Identify and validate alternative wood treatments <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative treatment chemicals — Test alternative treatment chemicals
Pigments and oxides	Do not use a pigment or oxide	Identify and validate alternative methods to avoid use of chromium or nickel containing pigments or oxides <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative approaches — Test alternative approaches
	Use nonhazardous pigment or oxide	Identify and validate alternative pigments or oxides <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative materials — Test alternative materials
	Minimize use of chromium or nickel pigment or oxide	Optimize coating application methods <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify improved application methods — Test improved application methods

TABLE 5. CHROMIUM AND NICKEL POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Pigments and oxides (continued)	Use non-chromium oxide recording media (e.g., metal powder tape)	Identify and validate alternative recording media <ul style="list-style-type: none"> — Reduce cost of metal recording media — Develop methods to prevent oxidation of metal recording media
	Avoid the use of chromium oxide recording media (e.g., optical data storage)	Identify and validate alternative data storage methods <ul style="list-style-type: none"> — Reduce cost of optical data recording systems — Increase flexibility of optical data recording systems
Battery manufacture	Replace nickel-based batteries and fuel cells	Identify and validate alternative materials for high performance electrodes <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative materials — Test alternative materials
Leather tanning	Use a less hazardous tanning agent	Identify and validate vegetable or other tanning agents that give leather quality similar to chromium tanning

POLLUTION PREVENTION OPPORTUNITIES AND SUPPORTING RESEARCH NEEDS

Plating for Hardness and Corrosion Resistance

Hard chromium plating is used to provide a working surface for a part. Chromium plating is the standard method for improving the hardness; smoothness; chemical inertness; or resistance to wear, abrasion, galling, or high temperatures for a wide variety of substrates. Typical applications are cylinder liners and pistons for internal combustion engines, cylinders and rams for hydraulic pistons, and extrusion equipment in plastic making (Guffie, 1986). Hard chromium plating will continue to be needed for specific applications, but alternatives are available for many of chromium's traditional applications. Design engineers will be required to be more selective in specifying hard chromium plating by exploring alternative technologies.

The hard chromium plating is electrolytically applied onto the substrate from an aqueous solution of chromic acid and sulfuric acid. The most common form of chromium in the plating baths is hexavalent chromic acid. Chromium metal is deposited on the substrate by a complex six-electron reduction of hexavalent chromium. The reduction reaction is catalyzed by the sulfuric acid. Plating from a hexavalent bath reliably produces a bright chromium plating. However, the current efficiency, the quantity of chromium deposited per unit of electric energy used, the throwing power, and the ability to produce a uniform coating over a large area are low. Hydrogen produced by the plating operation can migrate into the metal substrate and embrittle it. The use of hexavalent chromium involves operator exposure to chromic acid — a toxic material — and requires treatment and disposal of chromium waste.

The most commonly sought property for engineering nickel coatings is corrosion resistance. However, nickel plating also provides wear resistance, solderability, magnetism, and other properties needed in specific applications. Nickel plating is applied to protect chemical, pulp and paper, and other similar process equipment that must survive in corrosive environments. Nickel is frequently used as an undercoat for chromium plating where the chromium provides a hard bright surface and the nickel gives good corrosion resistance. Nickel plating is also used to salvage worn, corroded, or incorrectly machined parts.

Nickel plating involves deposition of a layer of nickel on a substrate. During deposition of nickel metal on the cathode, the nickel anode dissolves. Direct current flows through a solution of nickel salts to drive the reaction. Nickel is present in the solution as divalent ions that are converted to nickel metal at the cathode. The nickel in the bath is replenished by dissolution of the anode, so nickel plating can typically operate for long periods without interruption. Anode efficiency for nickel plating is typically 100%, whereas the cathode efficiency is

slightly lower. As a result, the nickel concentration in the bath increases with use, and periodic adjustments to the bath concentration are required. Chloride, sulfate, sulfamate, and fluoroborate are the most common nickel salts used in the plating baths. Nickel coatings for engineering purposes are usually prepared from solutions that deposit pure nickel.

Use an alternative substrate that does not need chromium or nickel plating. It may be possible to use an alternative substrate to provide sufficient hardness or corrosion resistance. For example, advanced ceramic and composite materials have been tested as replacements for metal parts in internal combustion engines.

Use nonaqueous plating for chromium or nickel pollution prevention. If an alternative substrate is not available, it may be possible to produce a coating with the necessary properties without plating from an aqueous bath. Hard coatings can be applied by physical vapor deposition (PVD). For example, titanium nitride is used as a coating to improve the wear resistance of cutting tools.

PVD coatings are applied in a vacuum chamber. A cleaned piece of substrate material is placed in a heated vacuum chamber. A gas plasma or electric arc heats and vaporizes the metal that is to be plated onto the substrate. The vaporized metal ions are deposited onto the substrate as a thin hard film (Gresham, 1991).

Plate with a less hazardous metal. Aqueous electroplating with less hazardous metals is another approach to reducing use of hard chromium or nickel plating. The electroplating operation is conceptually the same as chromium or nickel plating but, of course, uses different bath composition and plating conditions such as voltage and current. Possible alternatives include nickel-tungsten-silicon

Research needs. Research is needed to determine the performance requirements for hard chromium or nickel plating in specific applications and to identify test methods to measure the performance with respect to those standards. Then candidate substrate materials can be identified and tested as alternatives for hard chromium or nickel plating in specific applications.

Research needs. PVD coatings are generally harder and thinner than electrolytically deposited coatings. The major research need is to develop PVD coatings that give the required hardness and coating thickness, as well as other required performance characteristics, uniformly over a large complex part.

Research needs. The major research need is to develop replacements for chromium or nickel that give the required hardness and coating thickness, as well as other required performance characteristics, at a reasonable cost. Given the generally low current efficiency, deposition rate, and throwing power of hexavalent chromium plating, it is likely that alternative plating systems will give similar or better production rates.

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carbide plating (Schiffelbein, 1991) and molybdenum plating (Groshart, 1989).

Replace hexavalent chromium with trivalent chromium plating. There is a continuing trend in the chromium plating industry toward replacing hexavalent chromium baths with trivalent chromium baths, although trivalent plating is used mainly for appearance coatings rather than for hard coatings. The chromium chemicals used in trivalent plating are more expensive than those used in hexavalent plating. Some of the higher cost can be offset by the higher current efficiency and better throwing power of the trivalent process, as well as by selection of additives and process optimization to reduce costs.

Another impediment to wider acceptance of trivalent chromium is the color and finish achieved. Trivalent chrome gives a "gray" satin nickel appearance that is acceptable in many applications. While appearance should not be a major concern in most hardness and corrosion resistance applications, many customers prefer the "blue" finish typical of hard chromium plating from a hexavalent bath.

The anodes in trivalent chromium baths must be immersed in a non-chromium electrolyte solution held in a semipermeable membrane shield in the tank. The shielding prevents formation of hexavalent chromium at the anode. The shield occupies space in the bath that could otherwise be used for plating throughput (PsF, 1988).

Optimize traditional plating operations. If nickel or hexavalent chromium cannot be avoided, improvements can be developed to reduce waste in traditional nickel or hexavalent chromium plating operations (PsF, 1988).

Research needs. Research is needed to optimize trivalent chromium plating and expand its range of application. The major area of concern is to develop trivalent chromium plating methods that produce a coating with similar thickness, hardness, and color to hexavalent chromium plating. Methods to optimize the trivalent plating bath composition and operation to reduce costs are needed. Improved designs to minimize the volume required for electrode shielding are needed.

Research needs. Areas for research leading to improved plating operations include (1) using conductivity controls to minimize rinsing water use, (2) studying bath viscosity/temperature relations to optimize rates for solution draining from parts, and (3) studying the mixing effects to optimize plating tank agitation.

Recover or recycle plating solutions and rinse baths. Plating baths can be processed for reuse to decrease waste. Traditional separation processes can be used to recycle rinsing solutions or other baths that are no longer usable because of dilution but are not contaminated with undesirable impurities. However, the concentration or pH of the solutions may lead to challenges in equipment design or operation. If the solution is contaminated with impurities, more advanced ion-specific separation methods are needed to allow reprocessing.

Research needs. To expand the use of current separation methods such as evaporation, reverse osmosis, or ion exchange for processing spent plating solutions, research is needed to improve performance with high-salt-concentration, low-pH solutions (Walker et al., 1990).

To extend the useful life of contaminated plating solutions, new ion-specific separation methods need to be developed. Advanced selective ion separation methods to consider include advanced ion exchange resins, crown ethers, or membranes.

Plating for Appearance

Chromium plating is applied in some cases mainly to improve the appearance of the part. The plating solutions and procedures for appearance plating are similar to those for hard chromium plating. However, the operating conditions such as plating current and voltage are different.

Like chromium, some nickel plating has a mainly decorative function. Nickel plating appears on many commonly used items such as pins, paper clips, scissors, keys, and fasteners. Solutions used for appearance nickel plating have compositions similar to baths used for functional plating. However, baths used for appearance plating contain organic agents to modify the growth of the coating to control the surface finish of the nickel deposit.

Similar pollution prevention and recovery/recycling options are available for appearance plating. For example, plated parts could be replaced by brushed aluminum parts to eliminate the need for plating, a less hazardous metal could be applied to reduce the potential for pollution, or refractive plastics coatings could be used to eliminate metal plating. Because the appearance plating baths are similar, optimization and the bath recovery and recycling approaches for functional chromium and nickel plating will also apply. Appearance chromium and nickel coatings have lower wear resistance, corrosion protection, and thermal resistance requirements, so additional options are available for chromium and nickel replacement in appearance applications.

Use a non-chromium or non-nickel appearance coating. Because of the reduced performance requirements for appearance coatings, organic coatings such as refractive plastic or powder coatings can be acceptable.

Research needs. Research is needed to determine the performance requirements for appearance chromium or nickel plating in specific applications and to identify test methods to measure the performance with respect

to those standards. Then candidate coatings can be identified and tested as alternatives for appearance chromium or nickel plating in specific applications.

Surface Etching, Preparation, and Cleaning

Hexavalent chromium in the form of chromic acid is an inexpensive but powerful oxidizing solution. The oxidizing power of chromic acid solutions leads to a wide variety of industrial applications for cleaning and preparing surfaces.

- **Chromic acid deoxidizing/desmutting** — chromic acid is used to remove the natural metal oxide and other surface contaminants to prepare a surface for plating, painting, or other surface treatment.
- **Chromic acid etch** — chromic acid roughens surfaces to improve coating adhesion.
- **Chromic acid anodize** — anodizing is a process for treating aluminum to give a highly corrosion-resistant coating that offers an excellent surface for bonding and painting. Anodizing uses electrochemical methods to form a thin aluminum oxide surface layer that contains chromium ions.
- **Sealing** — Sodium dichromate as a sealant enhances fatigue properties by anodizing and by depositing oxydichromate onto the anodized layers.
- **Chemical film** — chromate solutions can be used to chemically deposit a thin film to prepare metal surfaces for subsequent painting (Evanoff, 1990).

Use alternative etchant for silicon wafer testing. Chromic acid is used to etch silicon wafers to reveal flaws in the crystal structure. The silicon wafers are the starting material for semiconductor circuits, so minute flaws must be reliably detected. Alternatives to chromic acid etching solutions are being developed and tested (Dickens and Cannon, 1991).

Use alternative oxidizing agents to prepare metal surfaces for coating or other use. Chromate solutions are used in a wide variety

Research needs. Research is needed to identify solutions that will provide adequate etching speed, give sufficient etching to meet or exceed current flaw detection requirements, and be compatible with the final use of the silicon wafer.

Research needs. Surface preparation alternative methods to treatment with hexavalent chromium need to be developed. The alterna-

of surface cleaning and pretreating processes. Several different formulations have been tested as alternatives to chromate solutions for surface preparation in a specific application (Bibber, 1991; Carrillo et al., 1991; Stewart, 1991).

tives must provide a surface layer with corrosion resistance, paint adhesion properties, impact resistance, and other anodic coating properties equal to those provided by chromate treatments.

Alloying

Chromium and nickel are common alloying additions in both nonferrous alloys such as chromium in StelliteTM or nickel in InconelTM and in ferrous alloys such as chrome and stainless steels. The addition of chromium and/or nickel increases the corrosion resistance and durability of the alloys.

Use non-chromium, non-nickel metal alloy or use a nonmetal alternative. It may be possible to develop other alloying agents to give the required wear, heat, or corrosion resistance. In lower temperature applications, it may be possible to use plastic or composite materials to replace chromium or nickel alloys. However, considerable effort by the nuclear industry searching for a replacement for StelliteTM has met with limited success. The manufacture of plastics and composites may generate organic solvent waste.

Research needs. Research is needed to determine the performance requirements for alloys in specific applications and to identify test methods to measure the performance with respect to those standards. Then candidates can be identified and tested as alternatives for chromium and nickel alloys in specific applications.

Increase recycle of high performance alloys. High alloy steels and superalloys are not readily recycled as mild steels. The alloying agents essentially become impurities in the steel making process when the alloys are recycled. It may be possible by increasing waste segregation and/or operating in smaller batches to increase the recycle of high performance alloys.

Research needs. Research is needed to determine the performance requirements for recycled alloys in specific applications and to identify test methods to measure the performance with respect to those standards. Then candidates can be identified and tested as alternatives for chromium and nickel alloys in specific applications.

Water Treatment Chemicals

Chromate salts, in combination with phosphate salts or other chemicals, are very effective for control of corrosion in low- and medium-temperature cooling water systems. These cooling systems typically contain several metals such as iron, steel, brass, copper, or aluminum. The range of properties of the materials of construction greatly complicates formulation of an effective corrosion-control additive package. Chromate-based additive packages have proven to be very

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stable and reliable for corrosion control in multimetal cooling water systems. Because of environmental concerns about chromate releases, many vendors are developing effective non-chromate cooling water treatment additive packages.

Expand use of non-chromium treatment chemicals. A variety of non-chromium additive packages are available and in use for specific applications.

Research needs. Research is needed to optimize and demonstrate available corrosion control additive packages in mixed metal cooling systems under a wide range of pH and oxidation/reduction potential conditions and high heat flux.

Refractories

Chromium is used in ceramic refractories for furnace lining materials that can resist high temperatures. Chromic oxide has very low solubility in molten glass, so chromic oxide bricks are used to line glass-making furnaces.

Use non-chromium refractories. It may be possible to develop refractory materials that do not rely on chromium additives to increase temperature resistance.

Research needs. Research is needed to determine the performance requirements for refractories in specific applications and to identify test methods to measure the performance with respect to those standards. Then candidate refractories can be identified and tested as alternatives for chromium-containing refractories in specific applications.

Catalysts

Nickel and chromium are used as catalysts in many industrial applications. Nickel catalysts find extensive application in the food processing industry for hydrogenation of edible and inedible oils. Nickel and chromium are essential in several steps in ammonia manufacture. Nickel catalysts are used in the primary and secondary reforming and methanation in ammonia production. Chromium catalysts are used in the high-temperature shift reaction in ammonia production. Combined nickel-chromium catalysts allow selective hydrogenation of olefins for use in ethylene manufacture. Nickel catalysts are also used for methanation of fuel gas in the petrochemical industry. Chromic oxide catalyzes hydrogenation-dehydrogenation reactions. Unlike metal oxides, chromic oxide will catalyze hydrogenation of both the C=O and C=C double bonds. Chromic oxide or various chromate salts can be used to catalyze the production of alcohols; dehydrogenation of alcohols; or hydrogenation of esters, aldehydes, and ketones.

Change synthesis path to avoid the need for a catalyst. Different combinations of chemical feedstocks may allow preparation of

Research needs. Research is needed to determine the requirements for specific reactions and to identify test methods to measure the

the desired product without the need for a catalyst.

Optimize the system to reduce catalyst use.

Improved reactor design or control can improve yields and reduce the need for catalysts. The classic continuous-stirred tank reactor may not be the best choice. Staged plug flow reactors can give better control of reaction conditions (Licis et al., 1991; Nelson, 1990). Guard beds could be used to remove poisons before the reacting mixture is sent to the catalyst process.

Improve reaction yield with the catalyst.

Design of the catalyst and its support will significantly affect the yield and product mix of the reaction and the resistance of the catalyst to poisoning. Changes in the formulation of the catalyst; how it is made; or its size, shape, porosity, and other physical properties can improve the performance of the reaction or increase catalyst life (Licis et al., 1991) and (Nelson, 1990).

Use a nonhazardous catalyst. It may be possible to identify alternative catalysts that give the same performance as chromium or nickel without increasing cost.

Recycle catalysts. Thermal and other regeneration techniques are available to remove poisons or otherwise process spent catalysts for reuse.

purity, yield, and other requirements. Then candidate reaction paths can be identified and tested as alternatives for paths requiring chromium or nickel-containing catalysts.

Research needs. Research is needed to optimize catalyst performance with specific reactions includes determining reaction kinetics, developing optimum reactor designs, and developing improved measurement and control systems. Research is needed to identify materials for guard beds to protect catalysts from poisons that degrade catalyst performance. The guard bed material would need to be compatible with the process materials, remove the poisons, and have low environmental impact.

Research needs. Research is needed to reduce the use of chromium or nickel catalysts by improving catalyst performance includes identifying and validating improved catalyst support matrices and developing catalysts with improved selectivity.

Research needs. Research is needed to determine the requirements for specific reactions and to identify test methods to measure the purity, yield, and other requirements. Then candidate nonhazardous catalysts can be identified and tested as alternatives for chromium- or nickel-containing catalysts.

Research needs. Research is needed to determine the requirements for specific catalyst recycle applications and to identify test methods to measure the purity, yield, and other requirements. Then candidate catalyst recycle treatments can be identified and tested as alternatives to extend the life of chromium- or nickel-containing catalysts.

Wood Treatment and Preservation

The wood preserving industry has been through several material changes to continue to provide durable wood products while reducing the hazards of treatment chemicals. The industry shifted from creosote to pentachlorophenol and most recently to chromated copper arsenate (CCA) for wood treatment.

Replace CCA as chemical treatment for wood preserving. Although an improvement over earlier wood preservatives, CCA still presents environmental concerns. Development of alternative treatments is desirable. One candidate is copper naphthenate (Licis et al., 1991).

Research needs. Research is needed to determine the performance requirements for wood preservatives and to identify test methods to measure the performance with respect to those standards. Then candidate preservatives can be identified and tested as alternatives for CCA.

Pigments and Oxides

Chromates are used to produce a wide range of yellow, orange, and green pigments. Zinc and strontium chromate pigments are used as corrosion-inhibiting priming coat under other paints. An expanding market for chromium oxide is as a component in the magnetic media in high-performance recording materials.

Black and green nickel oxides are used in the ceramic industry. Nickel oxide is added to ceramic formulations for porcelain enameling of steel to improve adhesion. Nickel oxides are also used in specialty ceramics such as nickel-zinc ferrites for magnets and nickel silicides for high-temperature electrical conductors. Various nickel compounds are used to color ceramic glazes. Organic nickel compounds are used as dyes.

Do not use a pigment or oxide. Methods may be available to avoid the need for chromium or nickel pigments or oxides.

Research needs. Research is needed to determine the performance requirements for chromium or nickel pigments or oxides and to identify test methods to measure the performance with respect to those standards. Then candidate materials can be identified and tested as alternatives for chromium and nickel pigments and oxides.

Use nonhazardous pigment or oxide. Alternative nonhazardous materials may be available.

Research needs. Research is needed to determine the performance requirements for chromium or nickel pigments or oxides and to identify test methods to measure the performance with respect to those standards. Then candidate materials can be identified and

Minimize use of chromium or nickel pigment or oxide. There may be ways to minimize the use of chromium or nickel pigment.

tested as alternatives for chromium and nickel pigments and oxides.

Research needs. Research is needed to determine the performance requirements for chromium or nickel pigments or oxides and to identify test methods to measure the performance with respect to those standards. Then candidate materials can be identified and tested as alternatives for chromium and nickel pigments and oxides.

Use non-chromium oxide recording media. Metal powder-based magnetic recording material is available; however, its use is limited by cost and problems with oxidation on the media.

Research needs. Research is needed to develop and validate methods to reduce cost and increase the corrosion resistance of metal powder magnetic recording media.

Avoid the use of chromium recording media. Methods such as laser disk data storage are available and could reduce the reliance on magnetic media for data storage.

Research needs. Research is needed to develop methods to reduce the cost and increase the flexibility of optical data recording systems.

Battery Manufacture

Porous electrodes made from nickel powder are used in rechargeable and high-performance batteries and fuel cells. Nickel-cadmium rechargeable batteries are used in many applications because they allow many discharge/charge cycles, have a long shelf life, and can be recharged quickly.

Replace nickel-based batteries and fuel cells. Alternative materials may be available for battery and fuel cell applications.

Research needs. Research is needed to determine the performance requirements for rechargeable and high-performance batteries and to identify test methods to measure performance with respect to those standards. Then candidate materials can be identified and tested as alternatives for nickel.

Leather Tanning

Tanning processes treat hides and skins to improve flexibility, durability, and resistance to microbial attack, producing leather that is useful for commercial applications. Chromium tanning gives a stable hide fiber which resists microbial attack and high temperatures. Chromium tanning is usually done in a single bath. In the single bath process, hides that have been soaked in an acidic solution of pH 3 are immersed into a solution of trivalent chromium salt, typically chromium

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sulfate. After the chromium salt penetrates into the hide, the pH is raised to cause the chromium to react with proteins in the hide.

Use a less hazardous tanning agent. Vegetable, aldehyde, and oil tanning can be used for limited applications but chromium tanning is still the most common process. The main advantages of chromium tanning are high processing speed, low cost, minimum discoloring, and good preservation qualities. It may be possible to improve vegetable or oil tanning to provide increased strength, acceptable color, and improved resistance to microbial attack.

Research needs. Research is needed to develop non-chromium tanning processes that give acceptable quality leather and good preservative properties.

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4 CYANIDE POLLUTION PREVENTION RESEARCH NEEDS FOR THE 33/50 PROGRAM

SOURCES AND PRODUCTION CHARACTERISTICS AND RATES

The name "cyanide" refers broadly to any molecule or ion that contains the carbon-nitrogen triple-bonded group $\text{-C}\equiv\text{N}$. This includes, for example:

- Hydrogen cyanide (hydrocyanic acid, prussic acid, formonitrile), HCN , which is a colorless, poisonous, low-viscosity liquid (melting point, or mp, -13.24°C ; boiling point, or bp, 25.70°C). Hydrogen cyanide is a weak acid ($\text{pK}_a=8.89$ at 18°C) and is not normally corrosive, with two exceptions: aqueous solutions can cause trans-crystalline stress-cracking of carbon steels, and aqueous solutions containing HCN and sulfuric acid as a stabilizer severely corrode steel above 40°C and stainless steels above 80°C (Kirk and Othmer, 1979).
- Alkali metal and alkaline earth cyanides are usually white, ionic, crystalline powders. Sodium cyanide, NaCN , is often called white cyanide. It is stable in water as an anhydrous salt above 34.7°C and as a dihydrate below 34.7°C . The solubility of $\text{NaCN}\cdot 2\text{H}_2\text{O}$ is 45 g (NaCN)/100 g solution, and decreases markedly with decreasing temperature. In aqueous solutions of NaCN , the cyanide ion is considered free, i.e., it does not completely form ion pairs with sodium ions. Free cyanide is quite toxic.
- Cyanide also forms strong complexes with iron, such as ferrocyanide and ferricyanide. Strongly complexed cyanides are resistant to breakdown and are low in toxicity.

Hydrogen cyanide enters the human body by inhalation, skin absorption, or orally. It is described as having the odor of bitter almonds, but one of five people cannot sense this odor, causing it to be all the more dangerous to them. Major uses of HCN are acrylonitrile, other nitriles, acrylates for plastics, and intermediates, such as for production of NaCN . Other products are ferrocyanides, chelating agents, optical laundry bleaches, and pharmaceuticals. Hydrogen cyanide is encountered as an industrial waste through the production of HCN and when other cyanide compounds are acidified.

Sodium and potassium cyanides are the only important alkali metal cyanides. As toxins, they behave similarly to HCN when taken orally or through the skin. They

can evolve HCN if exposed to moisture, such as in humid air. Sodium cyanide is used for gold and silver metallurgical extraction, pharmaceuticals, vitamins, plastics, ferrocyanides, and for electroplating of copper, zinc, cadmium, gold, and silver. Potassium cyanide is used in electroplating, and together with NaCN in nitriding steel, refining platinum, and in metal coloring processes. Calcium cyanide is the only alkaline earth metal cyanide used commercially. It is largely used in ore refining, for extraction and flotation, in the production of ferrocyanides for case hardening of steel, and also as a fumigant, rodenticide, and insecticide. See Table 6 for cyanide's pollution prevention needs.

Metal cyanides used commercially include nickel cyanide, which is used as a brightener in plating of other metals, and silver cyanide and zinc cyanide, which are used, respectively, in silver and zinc plating. In the plating process, these metals form complex cyanides, such as ferrocyanide and ferricyanide complexes with iron. Although these complexes are less toxic, they are also resistant to removal by treatment processes, and are decomposed by ultraviolet light, so that there is a possibility of generating HCN in waste streams containing cyanide complexes discharged by industry. Another waste source of cyanide is from spent pot liners used in aluminum refining.

Certain organic cyanides, called nitriles, are used as intermediates in chemical products and as a copolymer in plastics such as acrylonitrile/butadiene/styrene. The organic cyanide intermediates are not nearly as toxic as the inorganic cyanides.

POLLUTION PREVENTION OPPORTUNITIES AND SUPPORTING RESEARCH NEEDS

Electroplating

Cyanide waste generated in metal finishing comes primarily from copper, zinc, cadmium, silver, and gold plating, where large amounts of sodium and potassium cyanides and smaller amounts of metal cyanides are used. A considerable volume of wastewater is produced in the finishing industry. This waste usually contains dilute cyanide (10 to 770 ppm) from rinsing.

Due to process changes that do not use cyanide baths and the increasing use of cyanide recovery systems, cyanide waste is expected to decline greatly in the future.

TABLE 6. CYANIDE POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Electroplating	Use alternative to cyanide in plating processes	Expand use of silver succinimide- or lactide-based plating.
Mining and ore processing	Find replacement process for cyanide chemicals used in ore processing	Find alternative methods for ore separation.
Primary metals	Control release of cyanide in coking operations	Find methods to capture, process, and recycle HCN-containing gases from coking operations
Treatment processes	Improve electrolytic treatment process	Conduct research to improve the process <ul style="list-style-type: none"> — identify the means to convert more cyanide to cyanate — decrease the costs associated with chlorination
	Improve chemical oxidation treatment process	Improve oxidation kinetics of cyanide to cyanate
	Improve nonoxidation chemical treatment process	Conduct research to convert ferrocyanide products to stable nontoxic substances.
	Improve acidification treatment process	Conduct research to improve the efficiency of the "Cyan-Cat" process <ul style="list-style-type: none"> — convert a greater fraction of cyanide
Chemical intermediates and polymers	Eliminate CN use	Investigate the safety of operations in which HCN is handled
	Improve efficiency of process for producing polymers and chemical intermediates	Identify and evaluate processes that do not use CN in their production <ul style="list-style-type: none"> Improve efficiency of processes to prepare polymers and intermediates to reduce CN-containing waste to be treated

Use alternatives to cyanide in plating processes. Sodium cyanide is considered to be a multipurpose ingredient in many plating operations, but is especially important when plating the more noble metals. However, many alternatives are now being investigated for pollution control.

Research needs. Research is needed to develop non-cyanide processes that can provide acceptable performance features. Some examples of systems being studied are acid fluoroborate in cadmium plating, copper pyrophosphate or copper sulfate in copper plating, gold sulfite in gold and gold alloy plating, silver succinimide and silver sulfite/thiosulfate in silver plating, and acid chloride and alkaline noncyanide zinc baths for zinc plating.

Mining and Ore Processing

Sodium and calcium cyanides are used as a flotation depression agent in processing of copper, lead, and zinc ores. Cyanide complexing agents are used to extract silver and gold from ores. Cyanide is discharged with effluent water from mill tailings, which are usually untreated.

Find flotation modifiers and extractants to replace cyanide chemicals in ore processing. It may be possible to extract copper, lead, and zinc from their ores by a process that does not involve the use of cyanide.

Research needs. Research is needed to find alternative methods to provide flotation depression or extraction characteristics of cyanide salts in ore separation.

Primary Metals

Considerable amounts of cyanide are generated in steel production from coking operations and from carryover into blast furnace dust and sludges. Additionally, cyanide waste is generated in cold finishing of steel. In the aluminum industry, cyanides are generated in the process conversion of cryolite to aluminum metal.

Control release of cyanide in coking operations. Although recovery of HCN from coke-oven gases received little attention in past decades, environmental controls have spurred new research and development in this area (Ger. Pat., 1974).

Research needs. Research is needed to control the escape of HCN gases in coking operations.

Treatment Processes

A large number of treatment processes have been developed for cyanide treatment and destruction. Some of the known processes are as follows (Conner, 1990):

CYANIDE

- Electrolytic oxidation (U.S. Pat., 1972)
- Chemical oxidation (FMC Corp., 1975; Asturquimica, 1975; Zievers et al., 1968)
- Chemical reaction
- Acidification followed by HCN destruction ("Cyan-Cat") (Jola, 1976)
- Evaporative recovery
- Incineration or catalytic oxidation
- Gamma irradiation
- Reverse osmosis or electrodialysis (recovery)
- Carbon absorption
- Carbon bed catalytic destruction
- Foam separation
- Waste-plus-waste (Ottinger et al., 1973)
- Freeze-out (recovery)
- "Kastone" process (ES&T, 1971).
- Nascent oxygen
- Solvent extraction (recovery)
- Aeration
- Polymerization (U.S. Pat. 3,505,217)
- Starch process (U.S. Pat. 3,697,421)

Improve electrolytic treatment process. A considerable amount of research was done on anodic oxidation processes in the 1950s and 1960s. However, the effluent from this kind of treatment usually contains up to 10 ppm free cyanide and therefore must be given a follow-up treatment, such as by alkaline chlorination. This problem has made electrolytic oxidation uneconomical for dilute solutions.

A modification of this process has been proposed by Shockcor (1972, see U.S. Patent 3,692,661), in which the space between the anode and cathode is filled with carbon cylinders or spheres which act like a semiconductor bed to improve the conductivity of dilute solutions.

Improve chemical oxidation treatment process. The main problem is that although the reaction of cyanide to cyanate (which is about 1000 times less toxic) is fast, further oxidation of cyanate to carbon dioxide and nitrogen is

Research needs. Research is needed to improve the electrolytic process to convert more cyanide to cyanate and to decrease the costs associated with chlorination.

Research needs. Research is needed to improve the oxidation kinetics of cyanide to cyanate, such as by using a catalyst or other means.

quite slow. Also, chemical oxidation of complex metal cyanides is very slow because of their stability, so that the reactions may take hours to weeks to approach completion. In the Kastone process, organic glycolic compounds are formed that may require biological treatment before discharge. Furthermore, the presence of any oxidizable organic species will consume the oxidant and will be more costly.

Improve nonoxidation chemical treatment process. A variety of cyanide reactions can convert cyanide to less toxic substances or even commercially valuable compounds. One is the waste-plus-water method, in which ferrous sulfate waste at high pH is used to convert cyanide to ferrocyanide.

Organic polymerization, such as the reaction of cyanide with aldehydes at elevated temperatures to form nitriles and then hydrolyzed to amino acids, which are biodegradable. Starch conversion syrup has been used to produce a nontoxic reaction product.

Improve acidification treatment process. This process works by acidifying concentrated cyanide wastes with a strong acid, such as sulfuric acid, to decompose free and complex cyanides into other metal salts and HCN. The HCN is then stripped from solution in a desorption tower and catalytically oxidized in a thermal reactor to produce carbon dioxide, nitrogen, and water vapor (the "Cyan-Cat" process). The disadvantages are high capital cost, inherent dangers of producing HCN gas, and that dilute cyanide is left in solution, which must be removed by some other method. Advantages are that little auxiliary fuel is needed because the exothermic combustion of HCN provides almost all of the heat necessary for combustion (350 to 400°C).

Research needs. Research is needed to convert ferrocyanide products of the waste-plus-water process to stable, nontoxic substances.

Research is needed to improve the efficiency and economics of the organic polymerization methods.

Research needs. Research is needed to improve the efficiency of the "Cyan-Cat" process so that a greater fraction of cyanide is converted, and to investigate the safety of operations in which HCN is handled.

CYANIDE

Chemical Intermediates and Polymers

Important current uses of HCN include use in production of acrylonitrile, nylon (adiponitrile intermediate product), and methacrylate polymers (acetone-cyanohydrin intermediate in formation of methyl methacrylate monomer). In 1991, U.S. sales to major markets included:

• acrylonitrile	117 million lb
• acrylic polymers (only portions use cyanohydrin process)	672 million lb
• nylon	556 million lb
• Total nylon + acrylonitrile	673 million lb

For comparison, U.S. polyethylene sales to major markets totaled ~20,000 million lb (Modern Plastics, 1992). Recent research has targeted development of processes that avoid the use of HCN and improve process efficiency.

Use alternatives to HCN-produced chemicals. Chemical intermediates and polymers that are prepared using HCN in their production include some monomers and performance polymers.

Research needs. Research is needed to identify and evaluate processes to minimize the use of HCN in polymer production.

Control HCN-produced chemicals. Improved control of these processes would reduce risk and treatment needs.

Research needs. Research is needed to improve efficiency of processes to prepare intermediates and polymers to reduce CN waste.

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5 LEAD POLLUTION PREVENTION RESEARCH NEEDS FOR THE 33/50 PROGRAM

SOURCES AND PRODUCTION CHARACTERISTICS AND RATES

Lead (chemical symbol Pb) is a bluish-white, silvery, gray metal that is highly lustrous when freshly cut, but tarnishes when exposed to air. It is very soft and malleable; has a high density (11.35 g cm^{-3}) and low melting point (327.4°C); and can be cast, rolled, and extruded. Lead was well known in ancient times, and was extensively used because of its ease of fabrication.

Lead occurs in the earth's continental crust at concentrations of about 15 g/ton, or 13 ppm (Hurlbut and Klein, 1977). Although lead is a comparatively rare element in the earth's crust, lead ore deposits are unexpectedly numerous and widely distributed throughout the world. In addition to galena (PbS), which is the major ore mineral for lead, other source minerals include anglesite (PbSO_4), cerussite (PbCO_3), mimetite ($\text{PbCl}_2 \cdot 3\text{Pb}_3(\text{AsO}_4)_2$), and pyromorphite ($\text{PbCl}_2 \cdot 3\text{Pb}_3(\text{PO}_4)_2$). Lead is produced with other metals, such as zinc and copper, then smelted to remove impurities.

Of the estimated 1,400,000 tons of lead consumed in 1990, the U.S. Bureau of Mines (1991) has estimated apparent consumption patterns for lead as follows:

batteries	80%
ammunition	5%
non-battery oxides	4%
cast, sheet, or extruded products	4%
solder	1%
other uses	6%

About half of the lead used in the United State comes from recovery and reprocessing of scrap lead. The main sources of scrap are battery plates, drosses, skimmings, solders, babbitts, and cable sheathing. Of these secondary sources of lead, storage batteries make up more than half the total recovered. Channels for collecting used batteries are well emplaced, so that >90% are recovered for recycling.

Lead has two oxidation states, +II and +IV, with the former being more common. Pb(II) compounds are regarded as ionic, whereas Pb(IV) compounds are covalent.

Table 7 shows the pollution prevention research needs for lead.

TABLE 7. LEAD POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Emissions from primary lead smelting	Use an alternative lead production technology, e.g., leaching-electrolysis.	Investigate new developments in lead production technology.
Alloys	Use alternative material:	Explore the possibility for the conversion from batch to continuous modes of operation in future processes.
	— Use a non-lead alloy	Examine the properties of pure metals and alloys in order to determine if they may be adapted for use in place of lead alloys.
	— Use a ceramic material alternative	Examine the properties of advanced ceramic materials.
	— Use a plastic or composite alternative	Examine the properties of plastics and composites.
	— Use a non-lead solder	Examine the properties of metals having melting points near those of conventional solders.
	Eliminate the use of ancillary hazardous material from lead-alloy processes.	Improve the manufacture of electrical connections with the elimination of soldering.
	Optimize traditional alloying operations.	Conduct research to develop alternative methods for controlling the oxidation state of lead in the melt.
		Conduct research to find alternatives to arsenic in shrinkage prevention.
		Improve traditional processing operations.

TABLE 7. LEAD POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Alloys (continued)	Recover or recycle lead in alloying processes.	Conduct research to improve the performance of separation technology with the focus on ion-specific techniques.
Storage batteries	Use an alternative cell design	Research is needed to find new alternatives in electric power storage.
	Recovery of the lead components from the battery case.	Development of a recycling system to recover all lead-acid batteries.
Catalysts	Change synthesis path to avoid the need of a catalyst or use a nonhazardous catalyst.	Research is needed to determine the requirements for specific reaction pathways.
		— identify test methods to measure the purity, yield and other requirements of the syntheses product.
		— test the alternative reaction pathways.
		Identify and test nonhazardous catalysts as alternatives for lead-compound catalysts.
Electrical components	Avoid lead halide as a fluorescent coating in lamps	Find other fluorescent materials that can be used as a replacement for fluorescent and mercury vapor lamps.
	Redesign the lamps to exclude the use of lead halide as a phosphor.	
	Use a non-lead material in lead fuses	Study electric resistance and other properties of materials for use in fuses.

TABLE 7. LEAD POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Electrical components (continued)	Recover or recycle activator solutions for plating of nickel and other coatings	Research is needed to improve the performance of current separation methods with high salt concentrations and low pH solutions. Develop new ion-specific separation methods. <ul style="list-style-type: none"> — advanced ion exchange resins — crown ethers — membranes
	Replace the lead hydroxide in Ni-Cd batteries	Determine the performance requirements for rechargeable and high performance batteries <ul style="list-style-type: none"> — identify test methods to measure performance
	Minimize the use of lead pigments	
	Use nonhazardous materials for pigment	Determine performance requirements for lead pigments Find alternative substances that are nonhazardous
Paints and pigments	Use non-lead-containing metallic soaps	
	— Investigate Al, Ba, and Ca, as possible replacements	
	— Use other compounds to accelerate drying of paints and varnishes	Research is needed to study and test alternatives.

TABLE 7. LEAD POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Plastics and rubber	Use components other than lead compounds for stabilizers	Research is needed to find alternatives to nonhazardous substitutes for lead compounds
	Use other substances which can act as vulcanization accelerators	Explore alternative vulcanization accelerators in natural and synthetic rubber.
	Use nonhazardous materials for glazes and vitreous enamels	Determine the performance requirements for lead compounds for glazes and vitreous coatings.
Ceramics and glasses	Minimize lead compounds use	Find alternative nonhazardous substances.
		Find methods of improving performance without adding more lead.
		Find alternative substances
Specialty uses	Eliminate lead from lubricating grease	— determine what physical properties are imparted to lead-containing lubricating grease.
	Use a lead-free compound for insecticides and wood preservatives	Find suitable lead-free insecticides and wood preservatives.

Lead is an amphoteric metal, meaning that its oxides and hydroxides form both acidic and basic aqueous species. Almost all lead compounds are produced from pig lead to form lead monoxide, PbO , which is also called litharge. Other oxides of lead are PbO_2 , the mixed oxide Pb_3O_4 , and a black oxide (lead suboxide) that contains 60 to 80% PbO and the rest finely divided lead metal.

Lead and its compounds are cumulative poisons. However, because of its long history of use, more is known about lead poisoning than about poisoning by any other metal. Allowable lead levels have been established for drinking water, and various regulatory controls are in place for disposal of lead-bearing wastes. Lead is a probable human carcinogen, and it may also damage human chromosomes. It causes a range of systemic effects, including central nervous system and behavioral effects. It causes adverse acute and chronic effects in aquatic organisms and can be bioconcentrated.

POLLUTION PREVENTION OPPORTUNITIES AND SUPPORTING RESEARCH NEEDS

Emissions from Primary Lead Smelting

Smelting of lead ores is a source of lead emissions to the air, soil, and water. The primary method of lead smelting is the sinter-blast furnace method (Kirk and Othmer, 1979). Process modifications, such as using updraft sintering in place of downdraft sintering, have led to improvements in plant hygiene, as well as increases in output, economic production, and blast furnace performance. Still, overall problems in air pollution and waste disposal have led to the development of new approaches in lead smelting (AIME, 1979). Thermal inefficiency is inherent in the two-stage sinter-blast-furnace process. The heat generated by exothermic reactions should be adequate to reduce lead concentrates to metallic lead, but in practice additional fuel is needed. A one-stage process would be more efficient and would generate less waste. A number of one-stage processes have been commercialized or developed at the pilot scale (Matyas and Mackey, 1976). These include smelting lead concentrates and fluxes with oxygen-enriched air. Their products include sulfur-bearing bullion, slag, and a sulfur dioxide-rich gas.

Develop an electrolysis process to help eliminate air pollution. The U.S. Bureau of Mines has been investigating a hot iron chloride-sodium chloride leach-electrolysis technique to produce lead from galena. The filtrate contains > 99% of the lead, which is precipitated as lead chloride and electrolyzed to yield lead metal and chlorine gas.

Research needs. New developments of improving lead production technology should be investigated. These may include improvements and adaptations of traditional pyrometallurgical and electrefining processes. Conversion from batch to continuous modes of operation is a prime objective of future processes.

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Alloys

Lead is easily fabricated because of its softness, but it is not easily drawn because of its low tensile strength and absence of work-hardening at room temperature (Kirk and Othmer, 1979). Alloying is commonly done to add strength and other useful properties. The most commonly used elements for this purpose are copper (Cu), antimony (Sb), calcium (Ca), tin (Sn), arsenic (As), tellurium (Te), silver (Ag), and strontium (Sr). Bismuth (Bi), cadmium (Cd), and indium (In) are used less often for this purpose.

Lead-Copper Alloys. Alloying with copper produces considerable grain refinement and gives resistance to grain growth. Adding 0.04 to 0.08% copper (by weight) in lead, with or without the addition of silver, produces ASTM B 29-79 grades, which are suitable for sulfuric acid containment. Larger amounts of copper, 64% Cu (eutectic) or higher, are added in leaded brass or bronzes. General uses include stock for bearings and bushings in the automotive and aircraft industries, lead sheet, pipe, and wire. Lead-copper alloys are also used for continuous extrusion of lead cable coverings in electrical power cable. Extruded or rolled alloys contain uniformly dispersed copper particles that produce a self-passivating layer of lead sulfate on the alloy surface in sulfuric acid solutions.

Lead-Antimony Alloys. Lead-antimony comprises the most important class of lead alloys. Almost all lead products use antimony alloys in some fashion. Most commercial alloys contain 11.1% Sb (eutectic) or less. The solubility of antimony in lead decreases from 3.5% Sb at 252°C to 0.25% Sb at room temperature. This behavior allows Pb-Sb alloys to be precipitation-hardened by proper heat treatment procedures. The rate at which the alloy is cooled and its composition can be controlled to give a wide variety of mechanical properties. Like Pb-Cu alloys, Pb-Sb alloys develop a protective coating of lead oxide and lead carbonate that keeps them practically inert to further oxidative attack. Lead-antimony alloys are used for flashing material in roofing, and for making ammunition. Lead shot contains 0.5 to 8% Sb and has an arsenic content equal to about 20 to 30% of the Sb content. Arsenic is used to reduce any lead or antimony oxides present in the molten material and helps improve roundness of the globules during production; quenching is done by dropping the shot into towers of water. Shot larger than 5.8 mm and bullets are cast.

The principal use of Pb-Sb alloys is in the manufacture of grids, straps, and terminals for lead storage batteries. The antimony content of the lead alloy improves creep resistance and castability, which increase up to the eutectic point. It also provides a rigid strengthening network, which is important for hardness and stiffness of cast grids. Conventional automotive batteries use 4 to 6% Sb alloys for grids. New low-gassing, maintenance-free batteries use only 1.8 to 2.75% Sb. Large industrial batteries, deep-discharge batteries, and electric-vehicle batteries

use higher (5 to 9%) Sb contents. Internal connections and terminals are commonly made from a 3% Sb alloy.

Lead-antimony (0.5 to 1.0%) alloys are also used for cable sheathing, and provide higher strength and resistance to vibration than Pb-Cu alloys. The excellent strength of Pb-Sb alloy cables permit them to be reeled and unreeled and bent around corners without cracking or breaking.

Alloys with less than 3.5% Sb have structures that are highly susceptible to solidification-shrinkage porosity and cracking. This problem is overcome by the addition of nucleating agents, such as copper and arsenic, sulfur, or selenium.

Other uses Pb-Sb alloys include anode material for metal electrowinning and metal plating, collapsible tubes, and wheel balancing weights for automobiles and trucks, and specialty weights.

Lead Calcium Alloys. Low-calcium-lead alloys exhibit certain properties that give them advantages over traditional Pb-Sb alloys. Extruded Pb-Ca alloys are much stronger than either Pb-Cu or Pb-Sb (1%) alloys and have good ductility and excellent fatigue and creep resistance. Pb-Ca is used mainly as a grid alloy for large storage batteries because of its resistance to self-discharge and electrolyte loss upon standing and under full charge conditions. These alloys are increasingly being used for lead anodes in electrowinning, because they form a hard, adherent, corrosion-resistant layer of PbO_2 during use in sulfuric acid baths and greatly reduce lead contamination in the product. Alloys of 0.04 to 0.07% Ca are commonly used for these purposes, as well as for cable sheathing, sleeving, and specialty tapes. Further strength and performance improvements have been realized in the ternary system that includes tin, Pb-Sn-Ca, where 0.01 to 0.11% Ca and 0.3% Sn are used. Substitution of strontium for calcium in either the binary or ternary system improves strength.

Lead-Tin Alloys. Tin alloys have lead in all proportions, providing a wide range of alloy compositions for many different applications. Lead-tin alloys are mainly used as solders. Generally, lead-tin solders range in composition from 30 to 98% Pb. Pb(98%)-Sn(2%) solder is used to solder side seams of tin cans. However, substitution of 0.5% silver for Pb significantly improves creep strength, which is essential for pressurized cans. The high lead content and the practice of pretinning cans permit soldering to be performed at high speeds. General-purpose soldering is done with an alloy in the 40 to 50% tin range. Electronic soldering, as for printed circuit boards, uses Pb(37%)-Sn(63%) alloys. Solders in the composition range of 70 to 85% Pb are used for manufacturing automobile radiators and other kinds of heat exchangers.

Lead-tin alloys are also used as coatings on steel and copper for corrosion protection. Terne-coated steel is coated with an alloy of 80 to 85% lead. This

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composition gives good wetting and surface alloying with the steel. These coated sheets are used for radio and television chassis, roofs, fuel tanks, air filters, oil filters, gaskets, radiator components, metal furniture, gutters, and downspouts.

Alloys of Pb(96%)-Sn are applied to copper sheet for building flashing. Other alloys of Pb, in the 50% Sn range, are used to coat steel and copper electronic components for corrosion protection, appearance, and ease in soldering.

Lead and Pb-Sn coatings can also be applied by electroplating, usually from a fluoroborate solution. This method allows the coating to be applied in any desired thickness. Ordinarily, electroplated coatings are not used for corrosion protection, because they tend to be porous.

Lead-Antimony-Tin Alloys. The Pb-Sb-Sn system is an important series of alloys used in industry. Some materials made in this series include printing-type, lead-base sleeve bearings, special casting alloys, slush castings, and decorative casting alloys. These alloys are characterized by low melting points, high replication of detail in printing and mold in casting, and high wear hardness and strength, even at elevated temperatures. Kirk and Othmer (1979) provide properties of printing-type alloys and lead-base bearings. Pb-Sb-Sn alloys are also used in bushing and sleeve bearings, for their antifriction properties. They are used to make journal bearings in freight cars and mobile cranes. Arsenic and copper additives are also used to improve compression-, fatigue-, and creep-resistant properties at high temperature.

Lead-Silver Alloys. Lead-silver (0.75 to 1.25% Ag) alloys are used as insoluble anodes in zinc and manganese electrowinning. These alloys form a conductive layer of PbO_2 on the surface in sulfuric acid, which prevents lead contamination on the zinc or manganese coating.

Lead-Tellurium Alloys. Low tellurium (0.04 to 0.10%) alloys are used in fabrication of chemically resistant pipe and sheet. They are also used in materials for x-ray and nuclear radiation shielding.

Use a non-lead alloy. Non-lead alloys may be used to fabricate products that do not specifically require lead's physical properties to perform their functions. For example, bearings, bushings, pipe, wire, cable coverings, and flashing material may be constructed from metals that do not contain lead. Another example is to use alternative materials in place ofterne-coated steel for use in radio and television chassis. In addition, use another

Research needs. Research is needed to examine the properties of pure metals and alloys in order to determine if they may be adapted for use in place of lead alloys.

metal or alloy for casting and making printing-type.

Use a plastic or composite alternative. Products that do not require lead's electrical or physical properties to perform their functions may be fabricated instead from plastic or composite materials. Substitutions of this sort may be possible in low-temperature applications, such as decorative cast materials. Another example would be to use plastic or glass containers for food storage instead of metal cans, which have lead-solder joints. Use plastics or composites in place ofterne-coated steel for use in gutters, downspouts, and furniture. Use a high-impact composite material for making printing type.

Use a ceramic material alternative. An alternative substrate, such as an advanced ceramic, may be use in place of lead alloys for purposes of wear resistance or chemical inertness. For example, machine components such as bearings or bushings may be replaced by ceramics. Ceramic coatings may also be applied to base metals in order to be used for containing caustic chemicals.

Use a non-lead solder. Low-melting electrically conductive, corrosion-resistant alloys may be found in a non-lead system. Non-lead solders are now being used in household plumbing. Non-lead solders may also be used to form joints in canning. In electronics, some success has been found using electrically conducting epoxies in place of solder.

Eliminate ancillary hazardous materials from lead-alloy processes. Eliminate the use of arsenic by controlling oxidation of lead in melts using some other chemical or electrochemical method. Eliminate the use of arsenic

Research needs. Research is needed to examine the properties of plastics and composites in order to determine if they may be adapted for use in place of lead alloys.

Research needs. Research is needed to examine the properties of advanced ceramic materials in order to determine if they may be adapted for use in place of lead alloys.

Research needs. Research is needed to examine the properties of alternative metals to be used in place of conventional lead solders. Replacement solders must have melting points near those of conventional solders and possess similar flow and adhesion characteristics.

Research is needed to find and improve ways of making electrical connections without using solder. Electrically conducting epoxies already exist, but they have limitations.

Research needs. Research is needed to understand what redox conditions exist at melt temperatures, in order to develop alternative methods for controlling the oxidation state of lead in the melt.

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and selenium by controlling solidification shrinkage using sulfur or some other chemical additive. Prevent arsenic and selenium from entering the waste stream by careful attention of their use.

Optimize traditional alloying operations. If lead alloys cannot be avoided, improvements can be developed to reduce waste in traditional operations.

Recover or recycle lead in alloying process. Develop methods to remove impurities in lead alloys used for casting, plating, or other processes, to extend lifetime of the melt. For example, ion-specific separation methods may be needed to allow reprocessing.

Storage Batteries

About half of the total U.S. lead consumption is for manufacture of automobile and other storage batteries. A typical automobile battery contains the following component distribution:

lead alloy (5% Sb)	36%
lead oxides and sulfate	34%
case (hard rubber or polypropylene) and separators (PVC)	30%

Use an alternative cell design. The technology involved in the lead storage battery is fairly old and well entrenched in a number of important applications, for example in automobile electrical systems. Nevertheless, it may be possible to develop a different electrochemical cell that will meet the power storage requirements of modern internal combustion engines or of future engines.

Use recycling. To recover the lead components, several approaches have been used:

Research is needed to find what structural controls can be used in place of arsenic to prevent shrinkage.

An investigation of arsenic and selenium loss in lead production processes should be conducted to determine if greater concern should be attached to their usage.

Research needs. Areas of need may exist to reduce waste and improve recycling in traditional processing operations.

Research needs. Research is needed to improve the performance of separation technology. Ion-specific techniques may be used in this regard.

Research needs. This is a fairly mature technology that probably cannot be changed by a simple substitution of components. Research is needed to find new alternatives in electric power storage.

Research needs. A system for recycling can be created so that virtually all lead-acid batteries are recovered.

- (1) the battery case may be broken manually, the sulfuric acid poured off, and plates removed;
- (2) the battery case is crushed and screened, and the components are separated by density;
- (3) the complete battery is drained of acid smelted in a blast furnace; the organic components serve as fuel and as reducing agents.

Canonie Environmental Services, Inc., has recently developed a cleanup operation for the Gould Battery Superfund site in Portland, Oregon. A field demonstration involving 250 tons of material was processed using a 10-ton/hour unit (*HazTECH News*, 1992).

Catalysts

Lead compounds are used as catalysts in polymer manufacture and other reactions (Kirk and Othmer, 1979), for example:

- Lead fluoride is used in the manufacture of picoline, a pyridine compound (Ger. Offen. 1,903,879);
- Lead chloride is used as a co-catalyst for producing acrylonitrile (Fr. Pat. 1,556,127), and for polymerization of alpha-olefins to highly stereoregular polymers (Brit. Pat. 1,078,854);
- Lead carbonate catalyzes the polymerization of formaldehyde to high-molecular-weight crystalline poly-oxymethylene products (Jpn. Pat. 18,963);
- Basic lead carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$, or white lead, was once the major white hiding pigment before replacement with TiO_2 , but is still used for its catalytic properties for preparing polyesters from terephthalic acid and diols (Jpn. Pat. 64 20,533);
- Lead sesquioxide, Pb_2O_3 , is used as an oxidation catalyst for carbon monoxide in exhaust gases (Ger. Offen. 2,142,001; Ger. Offen. 2,156,414);
- Pb_3O_4 is used as a catalyst for combustion of carbon monoxide in exhaust gases.

In recent years, many producers have been pursuing non-lead components.

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Change synthesis path to avoid the need of a catalyst or use a nonhazardous catalyst. Different combinations of chemical feedstocks may allow preparations of the desired product without the need of a catalyst.

Research needs. Research is needed to determine the requirements for specific reactions and to identify test methods to measure the purity, yield, and other requirements. Then candidate reaction paths can be identified and tested as alternatives for paths requiring lead compounds as catalysts.

Electrical Components

Lead oxide, PbO, is most used in the manufacture of plates for lead-acid batteries. Other uses of lead compounds in electrical components include:

- Lead fluoride is used in making low power fuses (S. Afr. Pat. 68 04,061); activators for electroless plating of nickel on glass (Jpn. Kokai 74 27,442); electro-optical coatings (U.S. Pat. 3,745,044); and in zinc oxide varistors (Jpn. Kokai 74 14,996);
- Lead telluride and lead arsenate are used in making semiconductors and photoconducting devices;
- Lead zirconate titanate use for piezoelectric material;
- Lead chloride is used as a photochemical-sensitizing agent for metal patterns on printed circuit boards (U.S. Pat. 3,452,005);
- Lead iodide is used in mercury-vapor arc lamps (Fr. Pat. 1,467,694; USSR Pat. 457,121);
- Lead hydroxide is used in sealed nickel-cadmium battery electrolytes (Jpn. Kokai 75 16,045);
- Pb_3O_4 is used to make positive battery plates.

Use a different fluorescent gas in lamps. It may be possible to use a substance other than a lead halide to convert the mercury-vapor spectrum to visible light in fluorescent lamps.

Research needs. Research is needed to find a replacement for fluorescent lead iodide in mercury-vapor lamps, or to redesign the lamp without using lead or mercury compounds.

Use a non-lead material in electrical fuses. Find an electrically resistive, low-melting point substance to use in place of PbF_2 in low amperage fuses.

Research needs. Research is needed to study electrical resistance and other physical properties of materials for use in fuses.

Recover or recycle activator solutions for plating of nickel and other coatings. Solutions containing a lead halide can be processed for reuse to minimize waste. Traditional separation processes can be used to

Research needs. To expand the uses of current separation methods, such as evaporation, reverse osmosis, or ion exchange for processing spent plating solutions, research is needed to improve performance with high-salt-

recycle solution that are no longer usable, unless they are contaminated by impurities. If the solution is contaminated with impurities, more advance ion-specific separation methods are needed to allow reprocessing.

concentrations and low-pH solutions (Walker et al., 1990).

To extend the life of contaminated solutions, new ion-specific separation methods need to be developed. Advanced selective ion separation methods to consider include advanced ion exchange resins, crown ethers, or membranes.

Replace lead hydroxide in Ni-Cd batteries

Alternative materials may be available for battery electrolytes.

Research needs

Research is needed to determine the performance requirements for rechargeable and high-performance batteries and to identify test methods to measure performance with respect to those standards. Then candidate materials can be identified and tested as alternatives lead hydroxide.

Paints and Pigments

Lead compounds are not used as pigments in house paints any longer, since they have been replaced by titanium dioxide, which is not toxic. However, lead compound have historically been used in other areas of paint production as well.

- Pb_3O_4 (red lead) is used as an anticorrosive pigment in paint for steel surfaces;
- Lead chromate is used in high tint strength pigments (chrome yellow, chrome orange, and chrome green, a mixture with iron blue) for road paints, plastics, leather, and printing inks;
- Lead phosphates are used for high temperature and pearlescent pigments for plastics;
- Lead sulfide is used as a pigment in inks;
- A number of lead compounds, called metallic soaps, are added to paints and varnish oils to hasten their drying.

Use nonhazardous materials for pigment.

Alternative nonhazardous materials may be available for pigment to be used in paints, varnishes, and inks.

Research needs. Research is needed to determine the performance requirements for lead pigments and find alternative substances that are nonhazardous.

Minimize use of lead pigments. It may be possible to reduce the amount of lead oxide, or other pigment, used on a coating material.

Research needs. Research is needed to determine the performance requirements for lead pigments and to find methods of improv-

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Use non-lead-containing metallic soaps. A large number of metals are used in soaps, such as Al, Ba, Ca, Cu, Co, and Fe, in addition to Pb. Specific lead chemicals include lead tallage, lead naphthenate, and lead linoleate. It may be possible to use other compounds to accelerate drying of paints and varnishes.

ing performance without adding more lead pigment.

Research needs. Research is needed to find alternatives to metallic soaps for acceleration of paint and varnish drying.

Plastics and Rubber

Lead monoxide, PbO, is a component of heat stabilizers used for polyvinyl chloride resins, for which 8,616 metric tons of lead salts were used in 1979 in the United States (Smouluk, 1979). Specific lead compounds used in plastics include the following:

- Lead stearate is used as a vinyl stabilizer.
- Dibasic lead phosphate is used as a stabilizer for PVC to improve weathering resistance, thermal stability, and electrical insulating properties; some applications include garden hose, flexible and rigid vinyl foams, coated fabrics, plastisols, electrical insulation, and extruded profiles for outdoor use.
- Lead naphthenate is used as an accelerator for vulcanizing rubber.
- Lead dioxide, PbO₂, is used in the production of liquid polysulfide polymers (Greninger et al., 1975).
- Lead sesquioxide, Pb₂O₃, is used as a vulcanization accelerator for neoprene rubber (Jpn. Kokai 76 20,248).

Use components other than lead compounds for stabilizers. Elimination of lead in stabilizers would account for a large savings in lead usage.

Research needs. Research is needed to determine if there are nonhazardous materials that can be substituted for lead compounds to give PVC and other polymers their weathering resistance, thermal stability, and electrical insulating properties.

Use other substances that can act as vulcanization accelerators in natural and synthetic rubbers. Alternatives to lead sesquioxide and lead naphthenate, for example, may be found to accelerate vulcanization.

Research needs. Research is needed to explore alternative vulcanization accelerators in natural and synthetic rubber.

Ceramics and Glasses

After batteries, the next largest use for lead is in the ceramics industry in glasses, glazes, and vitreous enamels. The raw material, lead monoxide, or litharge, is used in ceramics and other industries. Lead monoxide combines with silicon dioxide to form a low melting silicate (Jpn. Pat. 69 18,745) that is used in the production of certain types of glazes and glass. When used as a glaze or vitreous enamel, lead oxides are converted to mono-, bi-, and trisilicate frits to make the lead compounds insoluble. Some other important lead compounds used in ceramics and their properties are as follows:

- Lead fluoride is added to glass coatings for infrared reflection (Ger. Offen. 1,421,872) and is used in phosphors for television screens (Ger. Offen. 2,106,118).
- PbCO_3 is a white pigment used in ceramics.
- Lead antimonate is used in tile painting, staining glass, crockery, and porcelain.

Use nonhazardous materials for glazes and vitreous enamels. Alternative nonhazardous materials may be available as coatings.

Research needs. Research is needed to determine the performance requirements for lead compounds for glazes and vitreous coatings and to find alternative substances that are nonhazardous.

Minimize use of lead compounds. It may be possible to reduce the amount of lead used in a glaze or vitreous coating.

Research needs. Research is needed to determine the performance requirements for lead compounds in coatings and to find methods of improving performance without adding more lead itself.

Specialty Uses

Lead compounds are used in a large number of industrial applications, for example:

- Lead oxide is used to make ammunition and detonating agents.
- Lead nitrite is used in explosives.
- Lead iodide is used in lubricating greases (U.S. Pat 3,201,347).
- Lead silicate is used in fireproofing fabric.
- Lead thiocyanate is used to make safety matches and cartridge priming.
- Lead naphthenate is used as a wood preservative and insecticide.

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- Sodium plumbite is used to remove sulfur compounds in petroleum refining.
- Lead arsenate and lead arsenite are used in insecticides for larvae of gypsy moth, boll weevil, and other insect larvae.
- Lead chloride (Brit. Pat. 1,235,100) and lead iodide (Brit. Pat. 1,235,100) are used to make asbestos clutch and brake linings.
- An aqueous paste of lead bromide is used as general-purpose welding flux for welding aluminum and aluminum alloys to other metals (U.S. Pat. 3,287,540).
- Lead chloride (U.S. Pat. 3,475,372) is used as a flame-retardant inorganic filler in polycarbonates.
- Lead bromide (Fr. Pat. 2,039,700) is used for flame retarding in polypropylene, polystyrene, and ABS plastics.
- Lead chloride is used as a flame retardant in nylon-6,6 wire coatings (U.S. Pat. 3,468,843).
- Lead dioxide, PbO_2 , is used because of its vigorous oxidizing power to make matches and pyrotechnics, and to produce certain chemicals.
- Lead bromide and lead iodide are used in film developing as an intensifier.
- Lead is used in wastewater filters to remove chromate.

Eliminate lead from lubricating grease. Use alternative substances in lubricating grease that will preserve the desired lubricating properties.

Use a substitute for lead compounds in flame-retardant and heat-resistant materials. Use alternative substances.

Use a lead-free compound for insecticides and wood preservatives. Find alternatives for insecticides and wood preservatives that are nonhazardous.

Research needs. Research is needed to determine what physical properties are imparted to lead-containing lubricating grease and to find alternative substances.

Research needs. Research is needed to understand how lead compounds behave to give materials flame retardant and heat resistant properties. Then, alternative compounds that are nonhazardous may be sought to give a material these same properties.

Research needs. Research is needed to find suitable insecticides and wood preservatives that do not contain lead.

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6 MERCURY POLLUTION PREVENTION RESEARCH NEEDS FOR THE 33/50 PROGRAM

SOURCES AND PRODUCTION CHARACTERISTICS AND RATES

Mercury (chemical symbol Hg) has been used since antiquity as a pigment and for medicinal purposes. The primary source of mercury is the sulfide ore, cinnabar. Mercury is also obtained in smaller quantities from ores containing mixed sulfides, oxides, and chloride minerals, which are usually associated with base and precious metals. Native or metallic mercury, is found in very small quantities in some ore sites. Mercury is estimated to occur in concentrations of 10 to 1,000 ppb in the earth's continental crust and 2,000 to 20,000 ppb in petroleum. By contrast, ore grade materials typically contain 5,000,000 ppb (0.5%) mercury. Some early methods for purification included leaching the ores in sodium sulfide and sodium hydroxide solutions, or in a sodium hypochlorite solution. Today, sulfide ores are retorted and liquid metallic mercury is condensed from the vapor.

Smaller amounts of mercury are produced from secondary sources, such as scrap batteries, lamps, switches, dental amalgams, measuring devices, and control instruments, and from laboratory and electrolytic refining wastes. Kirk and Othmer (1979) provide the quantity of mercury used in these types of products.

World production of mercury peaked around 1971 with annual production in excess of 10,000 metric tons; in 1978 production declined to about 6,000 metric tons (Kirk and Othmer, 1979). Production of mercury in the United States in those two years was 616 and 883 metric tons, respectively. This decline was due primarily to a drop in price, mining of lower grade ores, a decrease in consumer use, an increase in recycling, and curtailment of mining operations due to more stringent environmental protection regulations. The standard unit of trade is the "flask," which weighs 76 pounds.

Mercury consumption was reported in about 200 plants in the United States in 1988. Prime virgin mercury accounted for 66% of the total; secondary mercury, 27%; and redistilled mercury, 7%. Mercury usage increases in the manufacture of chlorine and caustic soda were reported in 1988. Other important uses include the manufacture of wiring devices and switches, which have declined steadily in the last decade, from 2,075 tons in 1984 to about 1,300 tons in 1990. Mercury use in dry-cell batteries has declined steadily in recent years.

The U.S. Bureau of Mines (1991) has approximated apparent consumption patterns for mercury in 1990 as follows:

electrical and electronic devices	33%
chlorine and caustic soda production	33%
instrument, dental, paints, and other uses	34%

Some of the first modern uses of metallic mercury were as a fluid in the barometer — Torricelli in 1643 — and the thermometer — Fahrenheit in 1720. Both devices rely on mercury's uniform volume expansion throughout its liquid range and its high surface tension that prevents it from wetting or clinging to glass. Today, mercury continues to be of technological value because of its unique properties that include high electrical and thermal conductivity, and high thermal neutron capture cross section, and its propensity to form amalgams, which it can do with almost every metal except iron (and iron too at high temperatures). Mercury compounds are no longer used as a biocide in interior latex paints but may still be used in some exterior latex paints.

Although mercury was known to be toxic for many centuries, the level of health hazard has come to light only since the 1970s. Metallic mercury, its vapor, and many of its compounds are protoplasmic poisons, which are toxic to all forms of life. Ingesting sufficient quantities, by mouth, through the skin, or by inhalation, can cause severe neurological damage and fatality in humans (Budavari, 1989). The alkyl organic compounds are the most toxic forms of mercury. Acute toxicity from mercury poisoning has on occasion manifested itself in catastrophic events. For example, 100 deaths or severe neurological damage resulted from consumption of fish in Minamata, Japan, contaminated with methyl mercury and mercuric chloride; another event in Iraq cause injuries from consumption of contaminated rice. It is now known that some marine organisms can biologically methylate inorganic mercury and concentrate it up to 3,000 times.

Table 8 shows the pollution prevention research needs for mercury.

TABLE 8. MERCURY POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Batteries	Improve efficiency of inhibitors	Conduct research on organic coatings used on Zn/Hg amalgams
	Search for new organic or metallic inhibitors	Explore new ways of inhibiting zinc oxidation or catalyzing hydrogen without diminishing the lifetime of battery performance.
	Develop longer lasting batteries	Improve existing battery technology.
	Encourage the use of rechargeable type batteries	Conduct research to discern the expected level of consumer participation .
Catalysts		Provide incentives for battery producers to market reusable batteries.
	Change synthesis path to avoid the need of a catalyst or use a nonhazardous catalyst	Research is needed to determine the requirements for specific reaction pathways.
		— identify test methods to measure the purity, yield and other requirements of the syntheses product.
		— identify possible alternative reaction pathways
Chlorine and caustic soda		Identify and test nonhazardous catalysts as alternatives for mercury-compound catalysts
	Use membrane cells for caustic soda production	Improve the electrolysis methods for conversion of sodium chloride to caustic soda and chlorine.

TABLE 8. MERCURY POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Switching devices and control instruments	Use alternative methods for sensing	Explore the existing alternative methods for replacing mercury instruments. — perform an economical analysis of the alternative candidates.
Electrical lamps	Use a different fluorescent vapor in lamps	Explore the electronic molecular properties of nonhazardous substances for use in fluorescent lamps.
Fungicides	Replace fungicide in exterior latex paint with non-mercury alternative	Search known bactericides and preservatives for a suitable alternative to fungicides containing mercury.

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POLLUTION PREVENTION OPPORTUNITIES AND SUPPORTING RESEARCH NEEDS

Batteries

Batteries make up the largest specific use of mercury, which in 1984 accounted for more than half of the mercury consumption in the United States (Kirk and Othmer, 1979). Mercury has historically been used to coat the zinc anode (negative electrode) in nonrechargeable household batteries. A few examples of these dry cell-type batteries are listed below:

<u>Battery Type</u>	<u>Size/Configuration</u>
Zinc-Carbon	AAA, AA, C, D, 9V
Alkaline-Manganese Dioxide	AAA, AA, C, D, 9V
Mercuric Oxide	Button cells (hearing aids)
Zinc-Silver Oxide	Button cells
Carbon-Zinc Air	Button cells (hearing aids and pagers)

Mercury is used to prevent the evolution of hydrogen gas from the battery, which results from internal chemical reactions. Hydrogen may pressurize the cell and cause internal leaking or explosion, although blowout valves are now installed at the tips to minimize this possibility. In the alkaline-manganese battery, zinc anodic material is added as a powder. In the past, 1 to 3% mercury was mixed with the powdered zinc to form a mercury-zinc amalgam that will inhibit zinc oxidation caused by chemical reactions with other components in the battery. The proportion of mercury in the amalgam decreases the rate of oxidation.

Alternatives to mercury have been sought within the battery manufacturing industry. Notable success has been found with some organo-silicate compounds. Testing by Rayovac (Tillman, 1991) has shown that these compounds restrict H_2 evolution. Results are listed below in order of increasing performance:

- sodium dimethylsiloxane \approx polydimethylsiloxane
- phosphate functional silate
- nonhydrolyzable silicone copolymer \approx polydimethylsiloxane-polyoxyethylene copolymer
- DC-193TM (proprietary compound)

The actual mechanism for restricting H_2 evolution is not known with certainty. Coating the zinc/mercury amalgam may form a physical barrier to diffusion, or it may increase mercury's efficiency in preventing zinc oxidation. Note that mercury is still used in this treatment, but smaller amounts are now needed. Batteries manufactured in the 1960s contained up to 1.3% mercury, by total battery weight.

An international standard set for implementation in 1992 calls for no more than 0.025% mercury.

Another development in mercury reduction in batteries has been reported by Battery Technologies Inc. (BTI, Mississauga, Ontario) (Roy, 1991). In developing a rechargeable alkaline zinc-manganese dioxide battery, they prepared "a cleaner, more precise (electrochemical) system" than is used in conventional single-use batteries. Their system claims to convert any hydrogen gas generated to water, and requires less mercury in the process. The BTI battery contains organic and other metallic inhibitors that perform the function normally assumed by mercury.

Improve efficiency of inhibitors. Improve the performance characteristics of the material used to coat zinc/mercury amalgams. Such improvements should permit less mercury to be used.

Search for new organic or metallic inhibitors. Use a different method of preventing zinc oxidation and subsequent H_2 evolution that does not involve zinc amalgamation with mercury. Following the example of BTI, mercury content should decrease to zero as the process is improved.

Develop batteries that last longer. Extend the lifetime of batteries so that they are disposed of less often. This proposal is based on the simple theory that a battery that lasts twice as long should end up in a landfill half as often.

Encourage use of rechargeable-type batteries. Rechargeable batteries will provide up to 20 times longer service hours than conventional single-use batteries. This option would translate into fewer batteries entering the waste disposal cycle.

Catalysts

Mercury ($HgCl_2$) is used as a catalyst primarily for the production of vinyl chloride monomers (Ulrich, 1988, p. 73) and urethane foams (Oertel, 1985, p. 114). It is also used to produce anthraquinone derivatives and other products. Discharges

Research needs. Research is needed to verify whether organic coatings on Zn/Hg amalgams work synergistically to improve the efficiency of the amalgam in restricting H_2 evolution.

Research needs. Research is needed to explore new ways of inhibiting zinc oxidation, or catalyzing H_2 to form water in a manner that does not diminish the lifetime of performance of the battery.

Research needs. Research is needed to improve existing battery technology so that batteries maintain a longer useful lifetime.

Research needs. Studies would first be conducted to discern the expected level of consumer participation in this pollution prevention strategy.

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from plants that produce these substances are sources of mercury-containing wastes. Old disposal areas may eventually require cleanup.

Change synthesis path to avoid the need of a catalyst or use a nonhazardous catalyst. Different combinations of chemical feedstocks may allow preparations of the desired product without the need of a catalyst.

Research needs. Research is needed to determine the requirements for specific reactions and to identify test methods to measure the purity, yield, and other requirements. Then candidate reaction paths can be identified and tested as alternatives for paths requiring lead compounds as catalysts.

Chlorine and Caustic Soda

Production of chlorine gas and caustic soda accounts for the largest use of mercury in the United States. The manufacturing process is also responsible for the largest loss of mercury into the environment. One process uses mercury and a following cathode in an electrolytic cell into which sodium chloride brine is introduced. A current is applied to electrolytically oxidize chloride anions to form Cl_2 gas, which is collected at the anode, and an alkali metal amalgam is formed with the mercury cathode. The amalgam is then decomposed with water to form caustic soda (sodium hydroxide) and hydrogen and relatively pure mercury metal. Although mercury metal is recycled back to the cell, large losses do occur in brine purification muds and in wastewater treatment sludges. The brine sludge contains small amounts of mercuric ions, mostly as the tetrachloro complex, HgCl_2^{2-} .

The membrane cell is another method of producing caustic soda and one which does not use mercury. The membrane cell uses cation and anion selective semi-permeable membranes to allow electrolytic separation of chlorine and caustic soda from brine. The membrane cell has advantages over the mercury cell that include lower operating voltage and higher efficiency, and it does not require the high capital investment in mercury.

Use membrane cells for caustic production. Improve the performance of membrane cells that do not require the use of mercury.

Research needs. Research is needed to better implement electrolysis methods for the conversion of sodium chloride to caustic soda and chlorine.

Switching Devices and Control Instruments

Mercury is used in high-/low-voltage mercury-arc rectifiers, oscillators, power control switches for motors, phanotrons, thyratrons, ignitrons, reed switches, silent switches, thermostats, and cathode tubes in radios, radar, and telecommunications equipment.

Mercury is also used in many medical and industrial instruments to control or measure reactions and equipment functions. This list includes mostly metallic mercury equipment, such as thermometers, manometers, barometers, the calomel electrode, and other pressure-sensing devices, gauges, valves, seals, and navigational controls.

Use alternative methods for sensing. There are some situations where electronically controlled devices can replace the role of mercury in mechanical instruments. For example, temperature can be detected using a thermocouple instead of a thermometer.

Research needs. Research is needed to explore what alternative methods exist for replacing mercury instruments and to judge whether they are economical to use.

Electrical Lamps

Mercury vapor is used in both the low-pressure "fluorescent" lamp and high-pressure mercury lamp. Fluorescent lamps are commonly used for indoor lighting, whereas high-pressure mercury lamps are used for street lighting, industrial work areas, aircraft hangers, and floodlighting. Other mercury-vapor lamps are used for photographic purposes, including motion picture projection, and for heat therapy.

Use a different fluorescent gas in lamps. It may be possible to use substances other than mercury for fluorescent lighting.

Research needs. Research is needed to explore the electronic molecular properties of nonhazardous substances for use in fluorescent lamps.

Fungicides

Mercury is used primarily in latex paint as a fungicide to prevent mildew of the applied coating and as a bactericide or preservative to inhibit bacterial attack during storage. The most commonly used fungicides are phenylmercuric acetate (PMA) and phenylmercuric oleate. Alkyl mercury compounds are no longer produced, due to their extreme toxicity and long lifetimes.

Mercury was used as a slimicide in the paper and pulp industry, but its use has decreased considerably since 1970.

Replace fungicide in paint with non-mercury alternative. Find alternative bactericides and preservatives that are compatible with exterior latex paint to extend storage life.

Research needs. Search known bactericides and preservatives for suitable alternatives to PMA and phenylmercuric oleate.

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7 POLLUTION PREVENTION RESEARCH NEEDS FOR ELEVEN TRI ORGANIC CHEMICAL GROUPS

SOURCES AND PRODUCTION CHARACTERISTICS AND RATES

Eleven organic chemicals have been selected from the Toxics Release Inventory (TRI) by EPA as target chemicals for the 33/50 Program. These include six chlorinated compounds (i.e., methylene chloride, chloroform, carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene) and five nonchlorinated compounds (i.e., methyl ethyl ketone, methyl isobutyl ketone, benzene, toluene, and xylenes).

Methylene chloride, chloroform, and carbon tetrachloride are chlorinated methanes. Methylene chloride, also known as dichloromethane, is a colorless liquid with a sweet, penetrating odor. It is manufactured primarily from the chlorination of methane (Budavari, 1989). Of the 452 million pounds used in 1988, paint stripping accounted for 28% of the consumption (*Chemical Profile*, 1989). Methylene chloride is also used for vapor degreasing (8.8% [*Chemical Profile*, 1989] or 20% [Ulrich, 1988]), cold cleaning, and food processing, as well as in the production of aerosols (20% [*Chemical Profile*, 1989] or 9.7% [Wolf et al., 1991]), urethane foam (10% [*Chemical Profile*, 1989] or 11.2% [Wolf et al., 1991]), adhesives, pesticides, electronics, pharmaceuticals, and textiles. Methylene chloride accounted for 10.9% of the 1988 TRI top 50 four-digit Standard Industrial Category (SIC) release and transfer (TRI R&T) (see Table 3).

Chloroform is a volatile, colorless liquid with a pleasant, sweet odor. It is manufactured from chlorination of methane or from reaction of acetone and bleaching powder with the addition of sulfuric acid. According to *Chemical Profile* (1989), chloroform consumption in 1989 totaled 484 million pounds. Of this, 90% was used for CFC 22 synthesis, of which 70% was used as refrigerants and the remainder in the production of fluoropolymers. Chloroform is also used for industrial degreasing and as a solvent for fats, oils, rubber, alkaloids, waxes, and resins (Budavari, 1989). Chloroform was once used as an anesthetic and in cough syrups and toothpastes; these uses have been restricted because of environmental and health concerns. Chloroform is also a chlorination by-product of some industrial processes, such as paper manufacturing. Chloroform accounted for only a small fraction of the 1988 TRI R&T, i.e., 1.9% (see Table 3).

Carbon tetrachloride is a colorless, clear, and sweet-smelling liquid. It is produced primarily by chlorination of either methane or carbon disulfide in the presence of a catalyst (Budavari, 1989). The consumption in 1988 was 761 million pounds. Of this, 91% of carbon tetrachloride was used for the production of chlorofluorocar-

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bons (CFCs) 11 and 12 (*Chemical Profile*, 1989). It is also used in the production of dyes, drugs, lubricants, and semiconductors. Carbon tetrachloride has been widely used as a household and industrial cleaning solvent and as a grain fumigant. These uses have been discontinued due to health concerns. As shown in Table 3, carbon tetrachloride accounted for about 0.4% of the 1988 TRI R&T.

The remaining three chlorinated compounds — 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene — are chlorinated C₂ chemicals. The basic feedstocks for these chemicals are ethylene, ethane, and propane. Chlorination of an intermediate — ethylene dichloride — yields a mixture of trichloroethylene and tetrachloroethylene. Chlorination of ethane yields trichloroethane, and chlorination of propane produces mixtures of tetrachloroethylene and carbon tetrachloride.

The first, 1,1,1-trichloroethane — also known as methyl chloroform or TCA — is a nonflammable liquid with a pleasant odor. In 1988, about 650 million pounds of TCA were used (Wolf et al., 1991; *Chemical Profile*, 1989), 52% of which was used in vapor degreasing and cold cleaning. TCA is also used in aerosol (13.5%), adhesive (8.7%), and coating (5.8%) formulations. TCA can be used as a photoresist developer and for printed circuit board defluxing and synthesis of hydrochlorofluorocarbon (HCFC). A smaller amount is used in textile processing, pesticide formulations, and flexible foam. TCA accounted for 13.5% of the 1988 TRI R&T (see Table 3).

Trichloroethylene (TCE) is a clear, volatile liquid with a sweet odor resembling that of chloroform. Its consumption in 1988 totaled about 160 million pounds (*Chemical Profile*, 1989; Wolf et al., 1991). TCE is used primarily in cleaning applications such as vapor degreasing and cold cleaning of fabricated metal parts (85% [Wolf et al., 1991; *Chemical Profile*, 1989]). Some TCE is used in the electronics and textile industries, and as a chain terminator in the production of polyvinyl chloride. TCE accounted for about 4% of the 1988 TRI R&T (see Table 3).

Tetrachloroethylene, also known as perchloroethylene or PERC, is a colorless liquid with an ethereal odor. The reported consumption of PERC in 1988 was 568 million pounds (Wolf et al., 1991), 46.5% (or 53% [*Chemical Profile*, 1986]) of which was used in dry cleaning and textile processing. PERC is also used in metal degreasing and cold cleaning (10% [*Chemical Profile*, 1986]), and as a solvent and a chemical intermediate in producing CFC-113 and CFC-114 (Wolf et al., 1991). PERC accounted for 2.7% of the 1988 TRI R&T (see Table 3).

Two ketones are included in the TRI target chemicals: methyl ethyl ketone and methyl isobutyl ketone. Methyl ethyl ketone (MEK) is a colorless, flammable liquid with an acetone-like odor. It is manufactured by dehydration of 2-butanol or by catalytic oxidation of n-butenes (Budavari, Inc., 1989). Its 1989 consumption totaled 429 million pounds. As summarized in *Chemical Profile* (1990), MEK is used primarily as a solvent for coatings (51%) and in adhesives (11%), magnetic

tapes (8%), and printing inks (3%). A smaller amount is used as an intermediate for a flavoring ingredient and as a solvent in nail enamel. MEK accounted for 11.3% of the 1988 TRI R&T (see Table 3).

Methyl isobutyl ketone (MIBK) is another colorless, flammable liquid with a pleasant, honey-like odor. It is derived by mild hydrogenation of mesityl oxide (4-methyl-3-penten-2-one). Its 1989 consumption was 156 million pounds (*Chemical Profile*, 1990). MIBK is used primarily as a solvent for protective coatings (60% [*Chemical Profile*, 1990] or 71% [Lawler, 1977]); a process solvent for adhesives, inks, and pharmaceuticals (10% [*Chemical Profile*, 1990]); in chemical production including rubber processing (10% [*Chemical Profile*, 1990]); and in the extraction of rare metals such as uranium from fission products (Sax and Lewis, 1987). It is used as a raw material for manufacturing antioxidants to improve the shelf life of some chemicals (Reilly, 1990). MIBK represented about 3% of the 1988 TRI R&T (see Table 3).

Benzene, toluene, and xylenes, often known collectively as BTX, are the basic feedstocks for many aromatic chemicals and polymers. Benzene is a volatile, colorless, and flammable liquid hydrocarbon with a slightly sweet aromatic odor. It exists naturally in crude oil and coal. It is manufactured or extracted in very large quantities in oil refining and coal coking (Kirk and Othmer, 1978). It is also produced from hydrodealkylation of toluene or as a by-product from steel production. In 1989, its consumption totaled 1,785 million gallons (*Chemical Profile*, 1990). Benzene is used primarily as a chemical raw material in the synthesis of ethylbenzene/styrene (53% [*Chemical Profile*, 1990]); cumene/phenol (21%); cyclohexane (12%); nitrobenzene/aniline (5%); detergent alkylate (3%); chlorobenzenes; and other products used in the production of drugs, dyes, insecticides, and plastics (Kirk and Othmer, 1978). Benzene has also been used in smaller amounts in gasoline and as a solvent and degreasing agent (Reilly, 1990), but these uses have been greatly reduced because of environmental and health concerns. Benzene represented 2.4% of the 1988 TRI R&T (see Table 3).

Toluene is a colorless, mobile liquid with a distinctive aromatic odor somewhat milder than that of benzene. It occurs naturally in crude oil, and 87% of toluene is produced by catalytic reforming of petroleum and subsequent fractional distillation of the aromatics (Sax and Lewis, 1987; Kirk and Othmer, 1983). (Toluene is usually produced along with benzene, xylenes, and C₉ aromatics.) Toluene may be separated from pyrolysis of gasoline produced in steam crackers during the manufacture of ethylene and propylene. It is also a by-product of styrene manufacturing. Consumption of toluene totaled 5,589 million pounds in 1984 (Ulrich, 1988). About 90% of the toluene generated by catalytic reforming is used as a blending component in gasoline. Toluene is an important feedstock for benzene manufacturing and a solvent in paints, coatings, adhesives, inks, pharmaceuticals, and other formulated products utilizing a solvent carrier. However, the use of toluene as a solvent in surface coatings is declining because

of various environmental and health regulations. Toluene represented about one quarter of the 1988 TRI R&T (see Table 3).

Xylene is a colorless liquid with a slightly sweet aromatic odor. Its three isomers, o-xylene, m-xylene, and p-xylene, coexist with ethylbenzene, and the mixture is usually called "mixed xylenes" (Kirk and Othmer, 1983). Mixed xylenes are derived mainly from catalytic reforming of petroleum (94.5%). Smaller quantities are produced from pyrolysis of gasoline (4.4%). Individual isomers are separated from mixed xylenes in oil refineries or petrochemical operations. In 1984, usages totalled 688, 90, and 2068 million pounds for o-xylene, m-xylene, and p-xylene, respectively (Ulrich, 1988). All three xylene isomers are important feedstocks for industrial polymers: o-xylene is mainly converted to phthalic anhydride, which is used for the synthesis of unsaturated polyester resins; p-xylene is oxidized to terephthalic acid and dimethyl terephthalate, which are the basic building blocks for synthetic polyester fibers and aramid fibers; m-xylene is converted to isophthalic acid for the manufacture of aramid fibers. Smaller quantities of xylenes are used as a solvent in paints, coatings, and agricultural sprays (Reilly, 1990). Xylenes accounted for 14.4% of the 1988 TRI R&T (see Table 3).

The pollution prevention approaches and research needs for the eleven organic chemicals are summarized in Table 9 and are outlined in the text following the table. Several points regarding the preparation of the table and the text are noted in the following:

- This document is prepared according to specific functions and uses of these chemicals rather than chemical classes. This is because chemicals in different chemical classes may be used for one specific application. For example, both chlorinated and nonchlorinated solvents are used for protective coatings and as cleaning solvents for printing. Most chlorinated methanes and chlorinated C₂ chemicals are used for vapor degreasing, cold cleaning, and paint stripping for metal surface preparation.
- The pollution prevention research needs are identified based on the technical information available in the public domain. Certain industries, such as chemical manufacturing and petroleum refining, do not provide information regarding specific pollution prevention techniques because of the diversity and specificity of the industries and the desire to guard confidential business information. Therefore, this document contains only limited discussion about the research needs for these industries.
- The research needs identified are applicable to most of the 12 two-digit SIC codes that are primarily responsible for the release of the target chemicals.

TABLE 9. ELEVEN ORGANIC CHEMICALS POLLUTION PREVENTION RESEARCH NEEDS

Function	Pollution Prevention Approach	Research Needs
Paint stripping	Avoid solvent use by plastic media blasting (PMB)	<ul style="list-style-type: none"> Improve work product quality and operating efficiency <ul style="list-style-type: none"> Assess long-term structural effects Determine substrate damage especially to composites Determine PMB effects on resistance of different substrates Evaluate PMB effects on substrate thickness to crack growth Evaluate potential for corrosion Evaluate potential for localized paint failure Determine cleaning requirements Determine PMB effects on substrate inspection
	Avoid solvent use by using bicarbonate of soda blasting	<ul style="list-style-type: none"> Improve work product quality and operating efficiency <ul style="list-style-type: none"> Determine potential for substrate damage Examine masking of fatigue cracks Examine effects of residual NaHCO_3 and its byproducts on substrate when exposed to operating conditions Optimize process conditions for thin-skinned aerospace structures Evaluate waste handling and disposal
	Avoid solvent use by using cryogenic blasting	<ul style="list-style-type: none"> Improve work product quality and operating efficiency <ul style="list-style-type: none"> Determine blasting effects on aircraft substrates Determine blasting effects on adhesive bonding materials Evaluate fatigue life degradation Evaluate crack growth potential Assess possibility of inducing microcracks in composites Optimize CO_2 pellet stripping process <ul style="list-style-type: none"> Pellet size, shape, and hardness Stripping pressure Impingement angle Stand-off distance Examine toxic airborne particulates

TABLE 9. ELEVEN ORGANIC CHEMICALS POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Paint stripping (continued)	Avoid solvent use by using laser or flashlamp to vaporize paints	Develop low-cost, high-power lasers or other light sources (Cheney and Kopf, 1990) Improve energy absorbance of light colored or glossy coating (Larson, 1990) Characterize and develop methods to control vapors produced
	Avoid solvent use by using other emerging technologies	Identify and validate new/emerging paint stripping methods <ul style="list-style-type: none"> — Define performance requirements — Determine process controls — Optimize process conditions — Evaluate effects on mechanical properties of parts — Evaluate waste reduction and pollution prevention potential — Assess economics
	Use alternative stripping agents	Identify and validate new stripping agents <ul style="list-style-type: none"> — Evaluate toxicity to environment and human health — Evaluate waste reduction and pollution prevention potential — Determine work product quality — Determine process controls — Optimize process conditions — Assess economics
	Use source reduction and recycling	Identify and validate methods to increase source reduction and recycling <ul style="list-style-type: none"> — Identify methods to reduce solvent usage — Identify opportunities to eliminate specific work steps — Identify methods to maximize stripping efficiency — Establish procedures to segregate wastes — Identify and validate methods to reuse or regenerate solvents <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Determine process controls — Optimize process conditions — Evaluate waste handling and disposal — Identify opportunities to recycle solvents

TABLE 9. ELEVEN ORGANIC CHEMICALS POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Solvent cleaning/degreasing	Avoid chlorinated solvents use by using aqueous cleaners	<p>Identify and validate aqueous cleaners (both commercially available and new)</p> <ul style="list-style-type: none"> — Identify and classify cleaners and soils — Establish cleaner evaluation criteria <ul style="list-style-type: none"> — Cleaning efficiency — Etch rate — Corrosion effects — Staining on substrates — Optimize cleaner performance <ul style="list-style-type: none"> — Drying of the cleaned parts — Determine specifications and production processes conformability — Evaluate emissions and chronic toxicity — Develop methods for cleaner regeneration and recycling — Determine waste handling and disposal — Assess economics
	Avoid chlorinated solvents use by using terpene- or glycol ether-based semiaqueous cleaners	<p>Identify and validate semiaqueous cleaners (both commercially available and new)</p> <ul style="list-style-type: none"> — Identify candidate cleaners — Establish evaluation criteria — Optimize cleaner performance — Determine specifications and production processes conformability — Evaluate biodegradability and toxicity — Evaluate emissions and chronic toxicity — Develop methods for cleaner regeneration and recycling — Determine waste handling and disposal — Assess economics

TABLE 9. ELEVEN ORGANIC CHEMICALS POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Solvent cleaning/degreasing (continued)	Avoid chlorinated solvents use by using aliphatic hydrocarbons such as mineral spirits, kerosene, white spirits, and naphtha	Identify and validate aliphatic hydrocarbons (both commercially available and new) <ul style="list-style-type: none"> — Identify candidate cleaners — Establish evaluation criteria — Optimize cleaner performance — Determine specifications and production processes conformability — Evaluate chronic toxicity and smog production potential — Develop methods for cleaner regeneration and recycling — Determine waste handling and disposal — Assess economics
	Avoid chlorinated solvents by using other new/emerging technologies (e.g., supercritical fluid cleaning, carbon dioxide snow, absorbent cleaning, vacuum degreasing, and cold catalysis)	Identify and validate alternative technologies <ul style="list-style-type: none"> — Establish evaluation criteria — Optimize cleaner performance — Determine specifications and production processes conformability — Monitor emissions and evaluate toxicity — Determine waste handling and disposal — Assess economics
	Use alternative cleaning processes that reduce or eliminate hazardous solvent usage	Identify and validate new processes <ul style="list-style-type: none"> — Establish evaluation criteria — Optimize cleaner performance — Determine specifications and production processes conformability — Monitor emissions and evaluate toxicity — Determine waste handling and disposal — Assess economics
	Perform process changes that eliminate cleaning	Identify and validate new processes <ul style="list-style-type: none"> — Establish evaluation criteria — Assess overall impact of process changes — Determine specifications and production processes conformability — Assess economics

TABLE 9. ELEVEN ORGANIC CHEMICALS POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Solvent cleaning/degreasing (continued)	Use source reduction and recycling	<p>Identify and validate methods to increase source reduction and recycling</p> <ul style="list-style-type: none"> — Identify methods to reduce solvent usage — Identify opportunities to eliminate specific work steps — Identify methods to maximize cleaning efficiency — Establish procedures to segregate cleaning wastes — Identify and validate methods to reuse or regenerate solvents <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Determine process controls — Optimize process conditions — Evaluate waste handling and disposal — Identify opportunities to recycle solvents
33 Solvent for coatings	Use alternative coating methods involving little or no volatile organic solvents	<p>Identify and validate alternative coating methods</p> <ul style="list-style-type: none"> — Determine performance requirements — Identify test methods — Identify alternative coating methods — Test new coating methods
	Use powder coatings as alternative coating methods	<p>Develop methods to apply thinner coatings particularly to complex-shaped or nonconductive substrates</p>
	Use high solids coatings as alternative coatings methods	<p>Identify types of formulations that provide the following while maintaining coating flexibility</p> <ul style="list-style-type: none"> — Coating adhesion — Flexibility — Impact resistance <p>Identify methods to optimize pot life versus curing time</p>
	Use water-based coatings as alternative coating methods	<p>Establish compatibility with metal substrates</p> <p>Examine corrosion effects</p> <p>Develop low-cost cleaning methods</p>

TABLE 9. ELEVEN ORGANIC CHEMICALS POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Solvent for coatings (continued)	Use UV-curing coatings as alternative coating methods	<p>Improve work product quality and operating efficiency</p> <ul style="list-style-type: none"> — Develop more advanced UV equipment — Identify new, nontoxic, low viscosity, 100% reactive monomers and oligomers that adhere to metal substrates — Develop new electronic and optronic resist materials — Evaluate coating service life — Assess material costs and process economics
	Use source reduction and recycling	<p>Develop new/modified equipment and processes that reduce solvent release</p> <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Test alternative equipment and processes — Determine costs
	Use source reduction and recycling	<p>Develop devices and methods that recover solvents</p> <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Test new devices and methods — Determine costs
	Use an alternative solvent	<p>Identify and validate a new solvent</p> <ul style="list-style-type: none"> — Define performance requirements — Develop testing methods — Test new solvent — Determine resource recovery and recycling possibility — Evaluate chronic toxicity — Determine costs
Dry cleaning	Use processes and equipment that eliminate solvent emissions, or use resource recovery and recycling	<p>Technologies matured and well developed, but research is needed to increase acceptance and application</p>

TABLE 9. ELEVEN ORGANIC CHEMICALS POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Blending components in gasoline	<p>Use an alternative blending chemical</p> <p>Improve fuel handling practices</p>	<p>Identify and validate new blending chemicals</p> <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify new blending chemicals — Test alternative blending chemicals <p>Identify and validate alternative gasoline dispensing methods</p> <ul style="list-style-type: none"> — Develop new fuel dispensing nozzles that eliminate or reduce fugitive emissions — Develop new fuel intake devices and that eliminate or reduce fugitive emissions — Develop new household gas storage tanks that eliminate or reduce fugitive emissions
Emissions from petroleum refining and related industries	<p>Systems analysis to reduce waste</p> <p>Improve source reduction and recycling practices to control emissions (U.S. EPA, 1992b)</p>	<p>Auto fuel emission screening</p> <p>Preheating catalyst to reduce auto emissions</p> <p>Microbial control using dilute halogen concentrations</p> <p>Spent caustic management</p> <p>Spent FCCU catalyst management</p> <p>Oily emulsion formation and control</p> <p>Reducing valve fugitive emissions</p> <p>Identify the source of the waste</p> <p>Identify methods and techniques to achieve source reduction and recycling</p> <ul style="list-style-type: none"> — Recycle hydrocarbon-bearing sludges from API separator to coking operation — Recycle used fluid catalytic cracking catalyst — Recycle spent caustic — Recycle wastewater treatment plant sludge to coking operation — Integrate units to reduce sludge generated from storage — Recirculate or recycling cooling waters — Recycle water used to cool and cut coke products

TABLE 9. ELEVEN ORGANIC CHEMICALS POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Emissions from primary metal smelting and refining	Control release of organics in metal smelting and refining	Find methods to capture, process, and recycle benzene-containing gases from coking operations Identify and validate new processes <ul style="list-style-type: none"> — Define performance requirements — Determine testing methods — Identify new processes — Test new processes — Evaluate economics and pay-back period Improve existing process control and modify equipment <ul style="list-style-type: none"> — Modify blast furnace to reduce coke requirements — Add coal tar decanter sludge to coking oven to reduce tar residue wastes — Use other process control improvement and equipment modification
Solvent for printing processes	Use substitutions to solvent-based inks and adhesives	Develop new inks and adhesives <ul style="list-style-type: none"> — Water-based inks — Soybean-based inks — Foamable aqueous inks — Water based-adhesives — Nonhalogenated adhesives — High solids adhesives Validate new inks and adhesives <ul style="list-style-type: none"> — Define performance requirements — Determine testing methods — Identify new materials — Test new materials — Evaluate costs
	Use nonhazardous cleaning solution	Identify and validate new cleaning solutions

TABLE 9. ELEVEN ORGANIC CHEMICALS POLLUTION PREVENTION RESEARCH NEEDS (Continued)

Function	Pollution Prevention Approach	Research Needs
Solvent for printing processes (continued)	Use source reduction and recycling	Determine source of wastes Identify methods to achieve source reduction and recycling Validate these methods
Solvent for rubber and miscellaneous plastic manufacturing	Avoid use of toxic solvents	Identify and validate new solvents <ul style="list-style-type: none"> — Define performance requirements — Develop performance testing methods — Identify alternative solvents — Test new solvents — Evaluate costs
	Use processes that do not use solvents	Identify and validate new processes <ul style="list-style-type: none"> — Evaluate impact — Evaluate costs and payback period — Define performance requirements — Test new processes
	Use source reduction and recycling	Identify and validate methods to increase source reduction and recycling <ul style="list-style-type: none"> — Identify methods to reduce solvent usage — Identify opportunities to eliminate process steps — Establish procedures to segregate wastes — Identify and validate methods to reuse or recycle solvents
Chemical manufacturing	Use generalize pollution prevention techniques for commonly used unit operations	Determine common unit operations and the pollution prevention techniques that may apply <ul style="list-style-type: none"> — Define performance requirements — Develop test methods — Test new methods — Develop cost information

POLLUTION PREVENTION OPPORTUNITIES AND SUPPORTING RESEARCH NEEDS

Paint Stripping

Paints and organic coatings are applied to surfaces of various substrates to enhance corrosion resistance and/or improve appearance. Often coatings need to be removed as part of the manufacturing operations or to enable maintenance or repair. In aerospace and aviation industries, coatings must be removed to allow inspection of underlying substrates for cracks and structural defects. Conventional paint stripping technologies use chemical or physical methods or a combination of both to remove paints. Chemical methods rely on the solvency, oxidizing, or swelling properties of the applied stripper to destroy coatings. Physical methods use abrasives, such as sandblasting, to scrape away paints. The chemical strippers most commonly used include chlorinated and aromatic solvents (e.g., methylene chloride and phenol-based solvents), caustic and acidic solutions, and molten salt.

Paint stripping operations generate large quantities of spent solvents and solvent-bearing wastewaters and solid-phase wastes. The operations also result in air emissions through volatilization during storage, fugitive losses during use, and direct ventilation of fumes.

Avoid solvent use. Several "clean" technologies that are either commercially available or are being developed, eliminate the use of hazardous solvents. These include plastic media blasting (PMB), bicarbonate of soda blasting, liquid nitrogen and carbon dioxide pellet cryogenic blasting, wheat starch blasting, ice crystal blasting, high-pressure waterjet stripping, and laser or flashlamp heating. These technologies remove coatings by using abrasive and/or impact action, extreme cold to embrittle coatings, or heat input to burn coatings.

PMB and bicarbonate of soda blasting use nontoxic plastic beads and sodium bicarbonate, respectively, as stripping media for coating removal. These processes do not generate noxious air emissions, but the disposal of the spent media could be a problem because they contain paint residues that often consist of hazardous metals or unreacted resins. Moreover, these processes are noisy and may generate toxic airborne particulates. The cryo-

Research needs. PMB is a more mature technology, but there are still areas that warrant future research. These may include long-term structural effects, PMB-induced substrate damage (especially to composites), and the effects of PMB on the resistance of different substrates and substrate thickness to crack growth (Cundiff et al., 1989). The cleaning requirements on different materials (e.g., clad aluminum, titanium, magnesium, stainless steel, and composites) after PMB (Galliher, 1989) and the effects of PMB on substrate inspection need further investigation. The potential for corrosion and localized paint failure also needs further study.

For bicarbonate of soda blasting, studies need to be done to determine the potential for substrate damage on sensitive materials, the degree of masking of fatigue cracks, the effects of residual sodium bicarbonate and its by-products on the substrate when exposed to

genic blasting uses liquid nitrogen or carbon dioxide pellets to embrittle coatings and subsequently remove them by PMB or carbon dioxide pellets. Cryogenic strippings result in a low-volume solid waste stream but still consisting of paint chips and spent plastic media. Wheat starch blasting uses particles of nontoxic, biodegradable wheat starch to remove coating. However, the fractured particles become less effective in coating removal, and the dust generated increases the explosion hazard. Ice crystal blasting results in a small volume of waste because ice crystals melt and evaporate. On the contrary, high-pressure waterjet stripping produces a large volume of aqueous waste. Laser and flashlamp coating removal use the thermal energy input from a laser beam and a xenon flashlamp, respectively. The last five technologies are mainly in the advanced pilot testing stage.

Use alternative stripping agents. Alternative stripping agents with less-toxic or nontoxic properties may be available to replace the hazardous stripping solvents. These stripping agents will be used to remove coatings from workpieces for which other mechanical stripping methods are not suitable.

Source reduction and recycling. There may be ways to extend solvent life and/or reduce solvent emissions to air, wastewater and/or solid-phase wastes.

operating temperature and humidity conditions, and the optimal process conditions for thin-skinned aluminum aerospace structures. The handling and disposal of the wastes also need to be evaluated.

Research is needed to determine the effects of liquid nitrogen cryogenic blasting on aircraft substrates and adhesive bonding materials, the long-term effects of the rapid changes in temperature on substrates, and the generation of toxic airborne particulates in the workplace. For carbon dioxide pellet blasting, further testing must be done on fatigue life degradation, crack growth potential, and the possibility of inducing microcracks in composite materials. Further optimization of the process is also needed for a wide range of substrates, including pellet size, shape, and hardness; pressure; impingement angle; and stand-off distance (Larson, 1990, Ivey, 1990).

Research is needed to identify and validate other new and emerging nonsolvent paint stripping methods. Studies should focus on the assessment of method effectiveness, the ability of achieving satisfactory work products, optimization of the process conditions, the benefits of waste reduction and pollution prevention, and the economics.

Research needs. Research is needed to identify less-toxic or nontoxic stripping agents for workpieces that cannot be stripped using the nonsolvent methods. The effectiveness of the stripping agents, the quality of the work products, the waste reduction potential, and the economics are the major items to be examined.

Research needs. When an alternative does not exist, source reduction and recycling may be used to extend solvent life and/or reduce solvent emissions (U.S. EPA, 1992a). Systematic studies are needed to identify methods to

reduce solvent usage, opportunities to eliminate specific work steps, methods to maximize stripping efficiency, procedures to segregate stripping wastes, methods to reuse or regenerate solvents, and opportunities to recycle stripping solvents.

Solvent Cleaning/Degreasing

Solvent cleaning/degreasing involves some of the most important steps during the surface preparation and finishing of the fabricated metal products. Cleaning/degreasing is performed to remove adsorbed substances that interfere with process performance or that affect product appearance. In metal finishing, the materials to be removed (usually called "soils") from the surface of a workpiece may include lubricants, cutting oils, polishing and buffing compounds, and oils for quenching and rust prevention. Other soils that may be encountered include rosin, solder fluxes, paints, adhesives, inks, toners, asphalt, particulates, and fingerprints.

Chlorinated solvents have been widely used to remove organic contaminants. The solvents most commonly used are trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), CFC-113, perchloroethylene (PERC), and methylene chloride. The classical cleaning processes involve vapor degreasing and cold cleaning. Vapor degreasing uses solvent vapor to contact the suspended soiled parts, dissolving the soil and flushing the liquid/soil mixture back into the hot liquid. TCE was once used as the prime vapor degreasing solvent, but because of its toxicity, its use has been largely replaced by TCA and CFC-113. Cold cleaning is usually performed in a tank containing TCA and other cleaning solvents at room temperature. The performance of the cold cleaning solvent usually degrades with use as it becomes loaded with dissolved materials.

The vapor degreasing and cold cleaning operations are major sources of emission of the chlorinated solvents. Air emissions through volatilization during storage, fugitive losses during use, and direct ventilation of fumes accounted for more than 80% of the 1988 TRI R&T (see Table 3). The degreasing and cold cleaning also produce large quantities of solvent-bearing wastewater and solid-phase wastes.

Avoid chlorinated solvents use by using alternative cleaning solutions. Nonhazardous or less-hazardous cleaning solutions can be used to replace the hazardous chlorinated solvents. Examples include aqueous cleaners, semiaqueous cleaners, aliphatic hydrocarbons, HCFCs, and N-methyl-2-pyrrolidone. Aqueous cleaners are made up of several classes of chemical components including builders,

Research needs. Before using an alternative cleaning solution, research is needed to identify and classify cleaners and soils, establish cleaner evaluation criteria, optimize cleaner performance, and determine its ability to conform with specifications and production processes. In general, an extensive industrial and/or literature survey must be conducted to identify candidate cleaners that are suitable for

surfactants, emulsifiers, deflocculants, saponifiers, sequestering agents, and/or other additives. Some aqueous cleaners have been in constant use by metal finishers, but the effects of various aqueous cleaners on different substrates have not been fully characterized. The drying of the cleaned parts also poses a challenge.

The semiaqueous cleaners are made up of biodegradable hydrocarbon solvents and water-based surfactants that form an emulsion upon mixing. The hydrocarbons used are usually terpenes (e.g., d-limonene, para-menthadienes, and terpene alcohols) and glycol ethers. The major uncertainty about the semiaqueous cleaners is their ability to meet biodegradability and toxicity requirements for economic recycling and disposal.

Aliphatic hydrocarbons include petroleum fractions such as mineral spirits, kerosene, white spirits, and naphtha. This technology becomes a viable alternative when water contact with the workpieces is undesirable. The chronic toxicity and smog production potential are among the subjects of concern.

Other chemicals that may be beneficial as a replacement solvent include alcohol, esters, glycol ethers, acetone, vegetable oils, and fatty acids. Many of these solvents have been used for some time.

In addition, supercritical fluid cleaning, carbon dioxide snow, absorbent cleaning, vacuum degreasing, and cold catalysis have also been suggested as new/emerging technologies to replace solvent cleaning and degreasing. All of these technologies need to be tested to determine their cleaning efficiency and their effects on substrates.

Use alternative cleaning processes. It is often possible to use alternative cleaning

the kind of soils (and substrates) to be cleaned. The cleaner evaluation criteria may include cleaning efficiency of each candidate cleaner, etch rate, corrosion effects, and staining on substrates. Adequate evaluation methods and techniques must be established for these evaluations and the optimization of the cleaner performance. The economics of the alternative cleaners must also be assessed before they can be fully accepted by industries.

When using an alternative cleaning solution, it is important to monitor emissions of cleaner components to workplaces and the environment and the associated chronic toxicity. It is also highly desirable to develop methods that extend solution life and reduce emissions. When considering solution regeneration and recycling, one must examine the cleaner performance both before and after the solution regeneration.

Research needs. The major research need is to identify and validate new process technolo-

processes to reduce or eliminate the need to use the hazardous chlorinated solvents or to employ technologies that eliminate the need for cleaning. Several cleaning processes are commercially available, including ultrasonic cleaning, automated aqueous washing, aqueous power washing, no-clean flux (low solids fluxes), no-clean solder. Ultrasonic cleaning uses conventional technologies, but tests must be performed to obtain the optimum combination of cleaning solution concentration and cavitation level. Automated aqueous washing and aqueous power washing combine an innovative process technology with the use of aqueous solutions. However, some delicate or difficult-to-clean parts may not be cleaned. No-clean flux and non-clean solder result in little or no visible residue on the integrated circuit boards; therefore, traditional flux may be eliminated. But even limited residues are sometimes not acceptable to many military specifications.

Other examples of process changes include surface cleaning by laser ablation, fluxless soldering, replacement of tin-lead joints, and temporary vapor storage (TVS). Research on TVS is being conducted based on the fact that it may be impossible to totally eliminate chlorinated solvent usage. Because regeneration of the carbon adsorbers that trap fugitive vapors from cleaning and degreasing operations often poses problems in terms of the operational efficiency and economics, systems such as TVS (Hickman and Goltz, 1991) do provide attractive features — utilizing an air lock and airtight equipment to allow temporary storage of solvent vapors from a solvent source and to return the vapors for reuse.

Source reduction and recycling. When chlorinated solvents must be used, there may be ways to extend solvent life and/or reduce solvent emissions to air, wastewater, and/or solid-phase wastes.

gies that could either reduce or eliminate the use of hazardous solvents or eliminate totally cleaning requirements during the fabrication/manufacturing processes. The process changes may involve the cleaning/degreasing or even the manufacturing processes.

Research needs. When an alternative does not exist, source reduction and recycling may be used to extend solvent life and/or reduce solvent emissions. Studies are needed to identify methods to reduce solvent usage,

opportunities to eliminate specific work steps, methods to maximize cleaning efficiency, procedures to segregate stripping wastes, methods to reuse or regenerate solvents, and opportunities to recycle cleaning solvents.

Solvent for Coatings

Paints and other coatings are applied to the surface of various substrates primarily to improve appearance and to resist corrosion. The substrates include sheet steel, plastic composites, stainless steel, aluminum, titanium, and wood. Examples of the industries applying coatings to these substrates include manufacturers of automobiles, aircraft, appliances, and wood products. Classical organic coating materials are dilute solutions of organic resins (e.g., alkyd, polyester, epoxy, polyurethane, acrylic, vinyl, and other resins); organic or inorganic (e.g., Cd, Cr, and Pb) coloring agents; and extenders dissolved in volatile organic solvents. The organic solvents, such as MEK, MIBK, benzene, toluene, and xylene, provide solvency, surface tension, and other properties to allow application of coating materials on substrate surfaces. The coating processes result in solvent waste, paint sludge wastes, paint-bearing wastewaters, and paint solvent emissions. Paint cleanup operations may contribute to the release of chlorinated solvents, such as carbon tetrachloride, methylene chloride, TCA, and PERC, and solid- and liquid-phase wastes from equipment washing, paint application emissions control devices, disposal materials used to contain paint overspray, and discarded paint materials.

Use alternative coating methods involving little or no volatile organic solvents. There may be ways to apply coatings without the use of volatile organic solvents. Examples include 100% dry resin formulations (powder coating), 100% reactive liquids (without any volatile components), water-dispersed or water-soluble polymer systems (water-based coating), or high solids polymer systems with reduced levels of organic solvents (high solids coating). In powder coating, a coating film is formed by applying either thermoplastic or thermosetting powders on the substrate surfaces and, subsequently, melting the powders in a fluidized bed or by electrostatic spray. High solids coatings use a higher concentration of solids with a lower concentration of volatile organic solvents, thus lowering fugitive solvent releases. Water-based coatings use water to replace or supple-

Research needs. Research is needed to identify new coating methods that eliminate the use of hazardous volatile organic solvents. It is also needed to determine the performance requirements for these new coating methods and to identify test methods to measure the performance with respect to these standards. The candidate methods can then be identified and tested as alternatives for coating.

For the existing technologies, studies are needed to improve the quality of work products, optimize the processes, and identify effects on human health and the environment. For example, for powder coatings, research is needed to develop methods to apply thinner coatings particularly to complex-shaped or nonconductive substrates. For high solids coatings, studies are needed to identify types

ment organic solvents. Ultraviolet radiation-cured coatings use high-intensity UV light to initiate free radical crosslinking of acrylate oligomers and prepolymers, thus eliminating solvent use and reducing paint waste. Several other technologies have also emerged as possible alternatives, including electron beam-cured coatings, radiation-induced thermally cured coatings, two-component reactive liquid coatings, water-based temporary protective coatings, vapor permeation- or injection-cured coatings, and supercritical carbon dioxide as solvent.

Source reduction and recycling. Methods may be available to reduce the release of volatile organic solvents through, for example, the use of new/modified equipment and processes and/or the recovery of the solvents from overspray. These pollution prevention approaches are especially useful for smaller size paint shops.

Dry Cleaning

Dry cleaning has been extensively used for the cleaning of fabrics. More than 70% of the dry cleaning is carried out with chlorinated hydrocarbons, including PERC, TCE, TCA, carbon tetrachloride, and fluorinated chlorohydrocarbons, among which PERC is the most widely used dry-cleaning solvent. Dry-cleaning washers usually consist of a metal shell and a rotatable perforated inner cylinder or wheel. The shell is a container for solvent, whereas the wheel holds the garment load. The spent solvents are purified by distillation or by activated charcoal and fatty acid-adsorbing sweetener powders. The solvent vapors are removed by a carbon adsorber, and the adsorbed solvent can be recovered by passing low-pressure steam through the adsorber.

Use an alternative solvent. It may be possible to use an alternative solvent to achieve

of formulations that provide good coating adhesion, flexibility, and impact resistance while maintaining coating flexibility. Methods to optimize pot life versus curing time are also needed. Because high solids coatings only reduce the amount of organic solvents in coating formulations, they may be considered only as near-term replacements for conventional coatings. In water-based coatings, studies are needed to establish compatibility with metal substrates and to address concerns over corrosion. Future work is also needed to develop low-cost cleaning methods for a cleaner surface for water-based coatings. UV-cured coatings need further development for more widespread future use. The specific areas are listed in Table 9.

Research needs. Research is needed to develop equipment and processes that reduce the release of volatile organic solvents. Examples include high-volume/low-pressure spray guns that replace the airless guns and processes incorporating prepainted automotive parts before assembly (Lietzke, 1992). Research is also needed to develop methods that recover volatile organic solvents from overspray.

Research needs. Research is needed to determine the performance requirements and

cleaning results similar to those by PERC and other hazardous solvents.

Use processes and equipment that eliminate solvent emissions or use resource recovery and recycling. If an alternative solvent is not available, it may be possible to develop processes and equipment that completely eliminate solvent emissions. It is also possible to recycle the spent solvents and recover fugitive vapors.

to identify test methods to measure the performance with respect to those standards. The candidate solvents can then be identified and tested as alternatives for dry cleaning.

Research needs. Technologies to achieve the pollution prevention goals are being developed. For example, the dry-cleaning industry has developed a dry-to-dry process to replace the old transfer method to handle the washed garment loads. However, research is needed to improve solvent recovery efficiency, reduce cost, and reduce worker exposure.

Blending Components in Gasoline

Toluene and some benzene have been used as blending components in gasoline, particularly in unleaded premium gasolines. As a blending component in automotive fuels, toluene and benzene have several advantages, including a high octane number, relatively low volatility, and the tendency to reduce engine starting difficulties (Kirk and Othmer, 1983).

Use alternative blending chemicals. It may be possible to use an alternative blending chemical.

Research needs. Research is needed to identify alternative blending chemicals that will provide an adequate octane number, relatively low volatility, and other desirable chemical properties. The performance of the chemicals will have to be evaluated for widespread use.

Improve fuel-handling practices. Devices and equipment may be developed to eliminate or reduce fugitive emissions of gasoline during automobile and household equipment refueling.

Research needs. Research is needed to develop new gasoline dispensing nozzles, automobile and household equipment fuel intake devices, and household gas storage tanks.

Emissions from Petroleum Refining and Related Industries

The primary emissions from petroleum refining and related industries are benzene, toluene, and xylene (U.S. EPA, 1992b). The individual process units responsible for these emissions include distillation, cat cracking, coking, and maintenance operation. The distillation process separates the crude oil components at atmospheric or reduced pressure by heating to temperatures of about 500°F and subsequent condensing of the fractions by cooling. Cat cracking breaks down larger, heavier, more complex hydrocarbon molecules into simpler and lighter

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molecules using controlled heat and pressure with catalysts. The coking process thermally decomposes heavier crude oil fractions to produce a mixture of lighter oils and petroleum coke. As for the chemical manufacturing industry, information relating to pollution prevention is not readily available.

Systems analysis to reduce waste. The Petroleum Environmental Research Forum (PERF), established in 1986 as a cooperative agreement among 24 petroleum companies, stimulates cooperative research for developing new environmental technology for the petroleum industry. Some of PERF's research programs and proposals reflect current research needs in the petroleum refining industry.

Improve source reduction and recycling practices to control emissions. Petroleum refining can result in various types of wastes and air emissions. It is important to identify the source of the waste before various source reduction and recycling techniques may be applied. The techniques to be used may include controlling fugitive emissions, source reduction and recycling of solid wastes, recycling process waters, and employing responsible maintenance practices.

Research needs. Research needs as reflected by the PERF research projects and proposals include auto fuel emission screening, preheating catalyst to reduce auto emissions, microbial control using dilute halogen concentrations, spent caustic management, spent fluidized bed catalytic cracking unit (FCCU) catalyst management, oily emulsion formation and control, and valve fugitive emission reduction.

Research needs. Research is needed to identify the source of the waste in each of the refining processes. Specific methods and techniques need to be identified to control fugitive emissions from sources such as crude oil and product storage tanks, coker, barge loading, etc. Methods also need to be identified/developed to achieve source reduction and recycling of solid wastes and process waters. Some areas of concern include recycling hydrocarbon-bearing sludges from API separator to coking operation, recycling wastewater treatment plant sludge to coking operation, and recycling water used to cool and cut coke products.

Emissions from Primary Metal Smelting and Refining

The major pollutants from the primary metal industry are benzene, toluene, and xylenes. These pollutants are produced primarily from heating coal in high-temperature coke ovens during coking operations. The coke oven gas is processed through recovery units to separate saleable by-products (e.g., benzene, toluene, and xylenes) and is then used as fuel. During cast or mold making, toluene and xylenes are used as mold washcoats. During hydrometallurgical refining, solvents can be used as extractants to recover metals from ores through leaching. The primary metal industry generates high-volume wastes including slags, off-gases, and process wastewater at all primary and secondary metal

smelting operations. The primary metal industry is a major source of TRI R&T (See Table 3).

Control release of organics in metal smelting and refining. For the primary metal industry, source reduction is a difficult task because all the chemicals of concern (except cyanide) come from the raw materials. Improved process control and equipment modification can decrease the amount or concentration of the VOC emissions, but do not entirely eliminate them. Changes in basic smelting and refining processes hold more potential to eliminate the wastes (U.S. EPA, 1992c).

Research needs. Research is needed to assess the impact of basic process changes on metal smelting and refining. Systematic studies must be carried out to determine the source of the waste and to develop new processes that replace the existing ones. For example, research is under way to develop direct iron and steelmaking processes that turn iron ore, coal, and limestone directly into iron or steel in one vessel, thus eliminating the need for coke ovens and blast furnaces (U.S. EPA, 1992c). Research is also needed to improve process control and modify existing equipment. Examples include modifying a blast furnace to reduce coke requirements and adding coal tar decanter sludge to the coking oven to reduce tar residue waste.

Solvents for Printing Processes

Toluene, MIBK, PERC, and TCA are used extensively during printing processes, causing their high releases to the environment. The chemicals are used as solvents in inks and adhesives, and as cleanup solvents. The wastes generated during plate processing, printing, and binding generally include solvents from heat-set inks, waste inks and ink sludges with solvents, cleanup solvents (including halogenated and nonhalogenated), and solvents from adhesive use.

Use substitutions for solvent-based inks and adhesives. It is possible to develop new nonsolvent-based inks and adhesives. For example, water-based inks have been developed for flexographic and rotogravure printing processes. Water-based (Randall et al., 1991), nonhalogenated, and high solids adhesives have been developed or the ideas have been suggested.

Use nonhazardous cleaning solutions. It may be possible to use/develop nonhazardous cleaning solutions or non-solvent-based cleaners.

Research needs. Research is needed to determine the performance requirements for the nonsolvent-based inks and adhesives and to identify test methods to measure the performance with respect to those standards. The candidate materials can be identified and tested as substitutions for printing and binding.

Research needs. Research is needed to identify and validate new non-solvent-based or nonhazardous cleaning solutions. The performance requirements and test methods need to

be defined and identified. New cleaning solutions will then be identified and tested.

Use source reduction and recycling. A variety of source reduction and recycling methods may be applicable to reduce or eliminate the releases of the toxic solvents.

Research needs. Research is needed to identify the source of the waste and adequate techniques that may achieve source reduction and recycling objectives.

Solvents for Rubber and Miscellaneous Plastic Manufacturing

Organic solvents are used during compounding, fabricating, and converting of the rubber and miscellaneous plastic products, and reclaiming of the waste materials. Rubber compounding involves mixing, calendaring, and vulcanizing; plastics compounding includes dry mixing of powders in a melt to produce pelletized or diced resin. Fabricating operations usually involve shaping and transforming rubber or plastic resin into a finished or semifinished product by molding, extrusion, or other fabricating methods. Converting operations involve removing the rubber or plastic overflow from the product before shipping. And reclaiming treats rubber wastes with heat and chemical agents and transforms the material to its original plastic state. These operations often produce spent solvents and fugitive solvent emissions.

Avoid use of toxic solvents. It may be possible to use alternative solvents in the production of rubber and plastic products.

Research needs. Research is needed to identify and validated new solvents to be used in the manufacturing of rubber and plastic products.

Use source reduction and recycling. There may be ways to limit the use of solvents and/or eliminate or reduce solvent emissions.

Research needs. When solvents must be used, source reduction and recycling techniques may be used to limit their use and/or to eliminate or reduce solvent emissions. Systematic studies are needed to identify methods to reduce solvent usage, opportunities to eliminate process steps, methods to reuse or recycle spent solvents, and techniques to recover fugitive vapors.

Chemical Manufacturing

All of the eleven TRI organic chemicals are used, in one form or the other, as basic feedstocks, intermediates, solvents, extractants, diluents, etc., in chemical manufacturing. The industry is typified by its diversity in the types of processes, techniques, and equipment used for both chemical manufacturing and pollution prevention. Because of the competitive nature of the business, the industry

usually uses its enormous in-house research and development resources and capabilities to develop specific pollution prevention methods for the manufacturing of a given product. However, the results of these efforts are usually not available to the public.

Use generalized pollution prevention techniques. There may be ways to minimize the release of hazardous organic chemicals during the chemical manufacturing processes. The best approach is to develop an understanding of whatever general pollution prevention techniques may apply to commonly used unit operations within the industry (U.S. EPA, 1992e).

Research needs. A considerable research program is needed to systematically study common unit operations and the pollution prevention techniques that may apply. The information obtained can be used to determine whether common industry usage of these techniques could result in more efficient pollution prevention.

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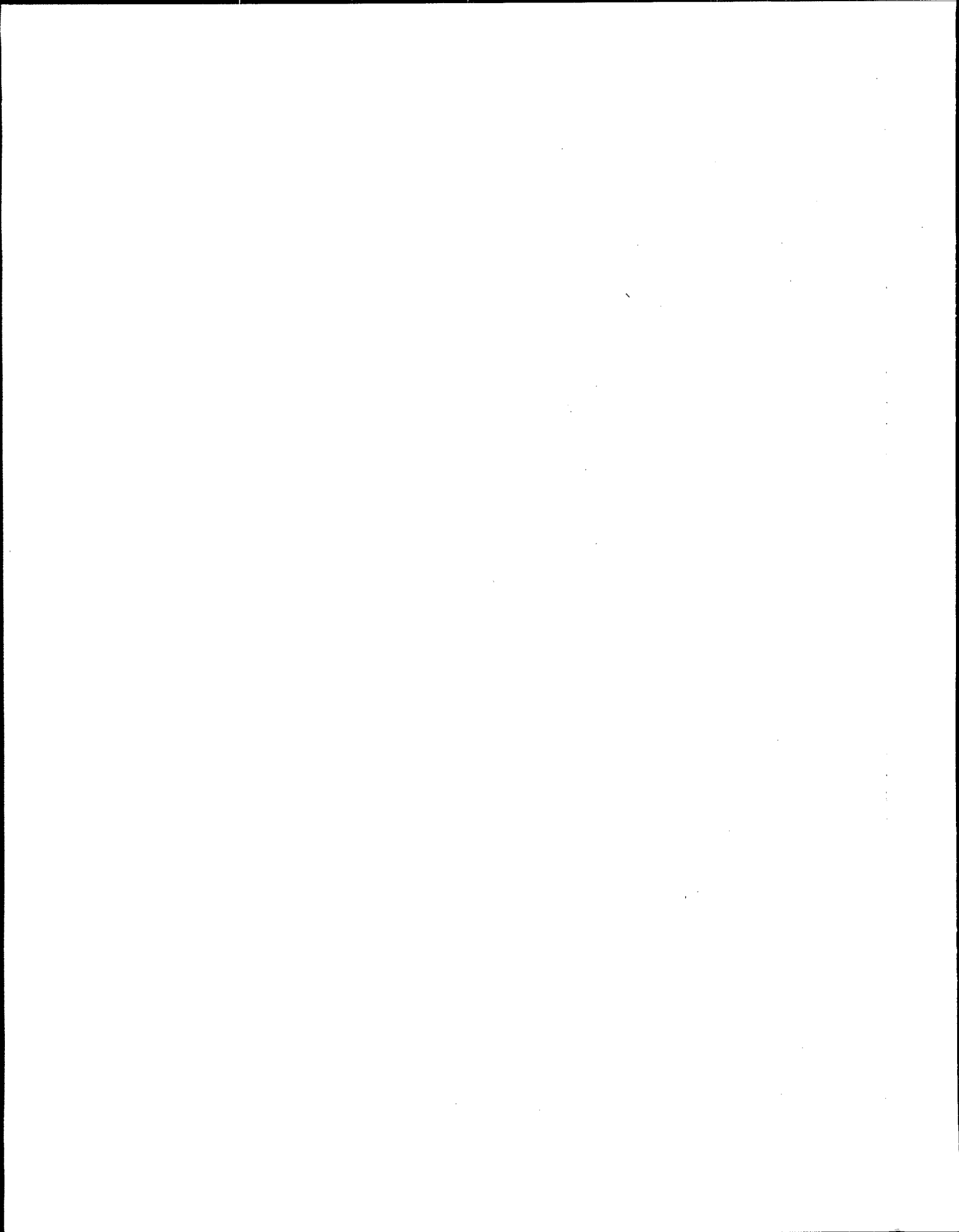
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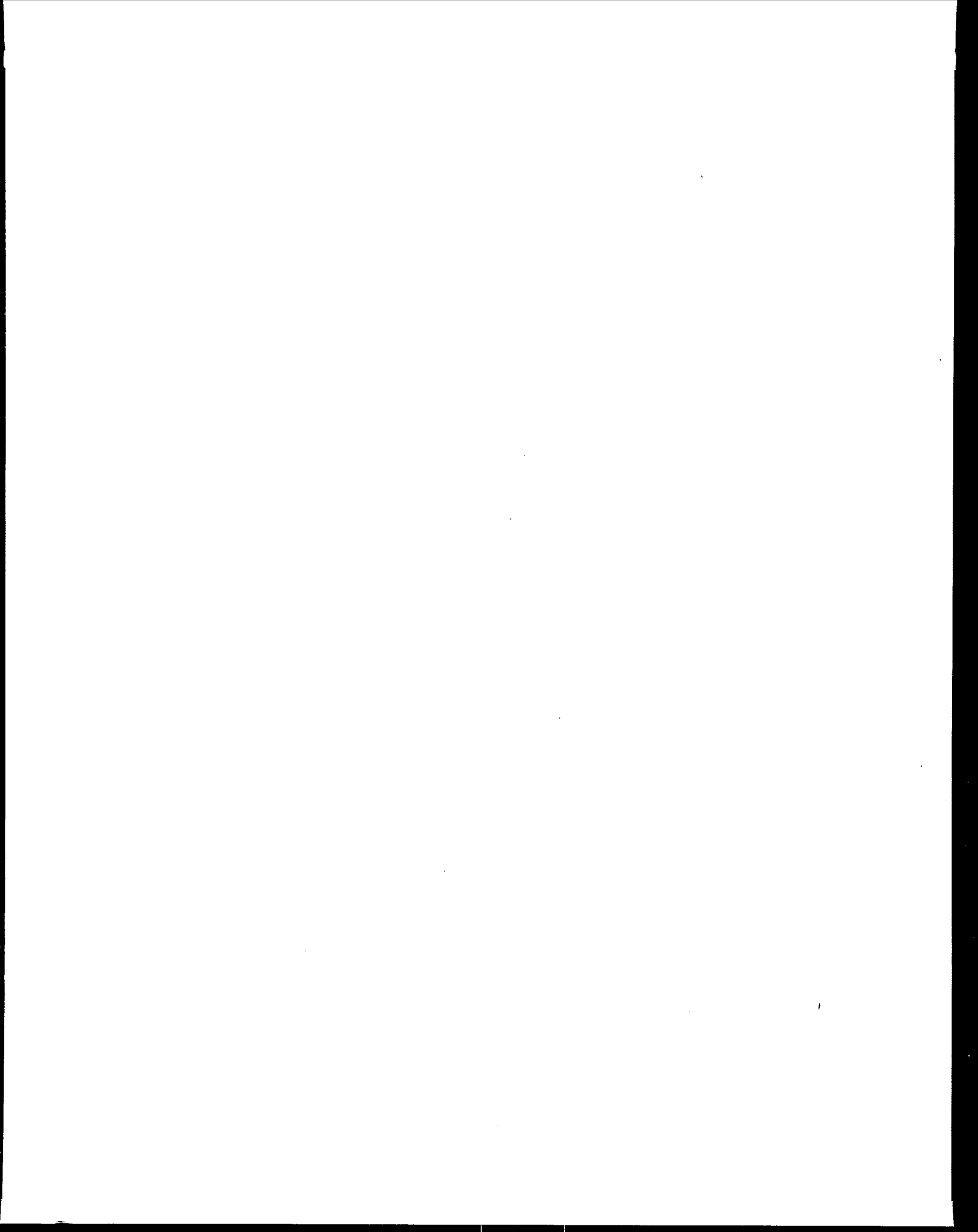
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