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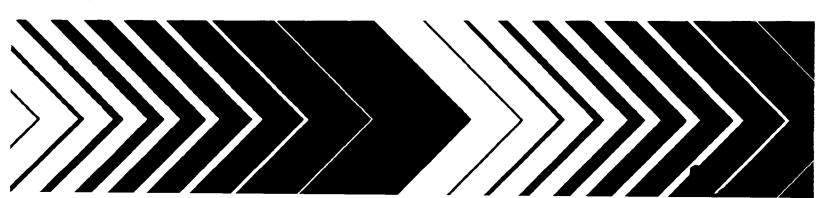
Research and Development



Status
Assessment of
Toxic Chemicals

6002792101

Mercury



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# STATUS ASSESSMENT OF TOXIC CHEMICALS:

MERCURY

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#### FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report contains a status assessment of the air emissions, water pollution, health effects, and environmental significance of benzene. This study was conducted to provide a better understanding of the distribution and characteristics of this pollutant. Further information on this subject may be obtained from the Organic Chemicals and Products Branch, Industrial Pollution Control Division.

Status assessment reports are used by IERL-Ci to communicate the readily available information on selected substances to government, industry, and persons having specific needs and interests. These reports are based primarily on data from open literature sources, including government reports. They are indicative rather than exhaustive.

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#### ABSTRACT

This report provides information on mercury, its sources and use, environmental significance, health effects, control technology, and regulatory action in progress. Approximately 1,900 metric tons/yr of mercury are available annually for domestic use. Sources of mercury include domestic ore smelting, secondary metal recovery, and imports. An estimated total of 1,525 metric tons/yr of mercury were lost to the environment in 1971 from mining and smelting of metals, manufacturing operations, fuel combustion, and use of industrial and consumer goods.

Mercury and many of its compounds are highly toxic; consequently, control technology has been implemented in the form of mist eliminators, wet scrubbers, direct and indirect condensers, and absorbers. Wastewaters containing mercury have been treated by sulfide precipitation, while sludges have been roasted under high temperature to remove mercury. Most control technology effectiveness is unknown.

Mercury has been designated as a priority pollutant for study under the Federal Water Pollution Control Act. Ocean dumping of mercury is prohibited except in trace amounts; the Food and Drug Administration has established a limit for mercury in edible fish of 0.5 mg/kg. Mercury ore refining and chloralkali plants are regulated to 2.3 kg of mercury emission for a 24 hr period.

Further studies are needed to determine the population which may be affected by mercury pollution. The efficiencies and cost of control technology should be ascertained if human health hazards caused by mercury exposure are to be avoided in an effective and economic manner.

This report was submitted in partial fulfillment of Contract 68-03-2550 by Monsanto Research Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period November 1, 1977 to December 31, 1977. The work was completed as of January 20, 1978.

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# **ABBREVIATIONS**

FDA -- U.S. Food and Drug Administration

MEM -- methoxyethylmercury

PMA -- phenylmercury acetate

ppb -- parts per billion

ppm -- parts per million

TLV -- threshold limit value

# CONVERSION FACTORS AND METRIC PREFIXES<sup>a</sup>

# CONVERSION FACTORS

To convert from	То	Multiply by
Gram/second (g/s)	Pound/hr	7.937
Kilogram (kg)	Pound-mass (pound-mass	
	avoirdupois)	2.205
Meter <sup>3</sup> (m <sup>3</sup> )	Foot <sup>3</sup>	$3.531 \times 10^{1}$
Metric ton	Pound-mass	$2.205 \times 10^{3}$
Metric ton	Kilogram	$1.000 \times 10^{3}$
Metric ton	Ton (short, 2,000	
	pound-mass	$1.585 \times 10^{-4}$

# METRIC PREFIXES

Prefix Symbol Multiplication factor		Multiplication factor	Example
Kilo	k	10 <sup>3</sup>	$1 \text{ kg} = 1 \times 10^3 \text{ grams}$
Milli	m	10 <sup>-3</sup>	$1 \text{ mm} = 1 \times 10^{-3} \text{ meter}$

<sup>&</sup>lt;sup>a</sup>Standard for Metric Practice. ANSI/ASTM Designation: E 380-76<sup>c</sup>, IEEE Std 268-1976, American Society for Testing and Materials, Philadelphia, Pennsylvania, February 1976. 37 pp.

# ACKNOWLEDGEMENT

This report was assembled for EPA by PEDCo-Environmental, Inc., Cincinnati, OH, and Monsanto Research Corporation, Dayton, OH. Mr. D. L. Becker served as EPA Project Officer, and Dr. C. E. Frank, EPA Consultant, was principal advisor and reviewer.

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# SECTION 1

# INTRODUCTION

Mercury and mercury compounds are utilized in many industrial processes and commercial products. The largest uses of mercury have been manufacture of electrical apparatus, industrial control instruments, and mercury-based pesticides.

All three common forms of mercury--elemental mercury, inorganic salts, and organic mercury compounds--all exhibit toxicological properties. Alkyl mercury compounds in the organic group appear to be the most hazardous. Methyl mercury can be formed from any of the three categories of mercury by microorganisms found in the bottom muds of aquatic environments.

The high toxicity of mercury has led to stringent regulations concerning mercury contamination; however, since its applications and environmental sources are diverse, mercury continues to enter the environment.

This report presents information detailing sources of mercury contamination, potential health effects, control technology, and regulatory actions. A brief description of the mercury production process is given along with the amount of mercury available from primary production, secondary production, and imported metal.

#### SECTION 2

#### SUMMARY

Major consumptive uses of mercury have included the manufacture of electrical apparatus, industrial control instruments, and mercury-based pesticides. The amount of mercury available for domestic use is approximately 1,900 metric tons/yr.<sup>a</sup> Mercury is obtained from primary processing of ore, secondary production from scrap, and imports.

Mercury and its compounds are generally toxic. Mercuric salts are fatal to man when taken internally at a dose of 20 mg to 3 g. Alkyl mercury compounds exhibit a high toxicity in man, causing death from injestion of several milligrams.

Major sources of mercury pollution include copper smelting, coal combustion, chloralkali production, control instrument manufacturing, and paint and battery consumption. Total mercury lost to the environment from all manmade sources was estimated at 1,525 metric tons/yr.

Control of mercury emissions in the primary smelting industry is accomplished by mist eliminators and wet-scrubbers. Secondary process industries control mercury emissions by direct and indirect condensation, chemical scrubbing, and adsorption. Wastewaters and sludges containing mercury have been controlled in the chloralkali industry by sulfide precipitation and by high-temperature roasting, respectively,

Mercury has been classified as a priority pollutant for study under the Federal Water Pollution Control Act. The U.S. Food and Drug Administration (FDA) has established a guideline for mercury in edible fish of 0.5 mg/kg.

Table 1 summarizes information on the sources and amounts of mercury contamination in the environment, its uses, and present control technology.

<sup>&</sup>lt;sup>a</sup>l metric ton equals 10<sup>6</sup> grams; conversion factors and metric system prefixes are presented in the prefatory material.

TABLE 1. SOURCES OF MERCURY, THEIR MAGNITUDE, AND CONTROL

		cury los			
Source	Air	Water	Land	Control technology	Regulatory action
Mercury mining and smelting	7.85	0	0.45		
Other mining and smelting:					
Copper mining	0.02	0.01	0.08	Mist eliminators and wet scrub-	Mercury ore process∸
Zinc and lead mining	0	0	0.01	bers control mercury in pri-	ing 2.3 kg/24-hr
Copper smelting	40.77	2.26	45.29	mary mining and smelting;	period.
Zinc smelting	4.59	0.25	5.09	Secondary metal processing	A 0.05 mg/m <sup>3</sup> threshold
Cement processing	0.5	0.25	2.51	industries use direct and in-	limit value (TLV) ha
Lime processing	0.08	0.04	0.41	direct condensation, chemical scrubbing, and adsorption.	<pre>been established for mercury in workroom air.</pre>
Unregulated sources:					dii.
Livestock	0	0	17.7	Combustion sources control	
Fuel oil consumption	16.94	0	0.02	particulates containing mer-	
Refineries	1.15	0	1.15	cury with electrostatic pre-	
Tars and asphalt	1.1	1.67	14.99	cipitators, wet scrubbers, and	
Coke ovens	7.16	0.51	2.56	baghouses.	
Coal combustion	9.97	0	1.11		
Utilities, oil, and natural gas	11.99	0	0.01		
Natural gas consumption	15.46	0	0.01		
Utilities, coal	40.71	0	4.52		
Manufacturing and processing:					
Caustic	0	7.61	1.9	Sulfide precipitation is used to	Chloralkali plants are
Catalyst manufacture	0	0.02	0	treat wastewater from chlor-	allowed 2.3 kg/24-hr
Paint manufacture	0.01	0.2	0.05	alkali plants. Sludges are	period (mercury emis
Pesticide manufacture	0	0.06	0	treated by high-temperature	sions). Mercury has
Pharmaceuticals manufacture	0	0.2	0	roasting.	been designated as a
Chloralkali	14.84	2.93			priority pollutant under the Federal
Textiles	0 0.29	0.15	7.63 0		Water Pollution Con-
Paint formulation Control instrument manufacture	0.29	0.35	1.97		trol Act.
Catalyst usage	0.05	0.1	18.85		A 0.05 mg/m <sup>3</sup> threshold
Tubes/switches manufacture	0.03	10.23	8.7		limit value (TLV) ha
Lamp manufacture	0.4	0	1.57		been established for
Battery manufacture	0.13	Ö	1.34		mercury in workroom
Other	10.28	0.05	2.49		air.
Commercial and industrial consumption:					
Urethane	0.12	0	2.22		A 0.05 mg/m <sup>3</sup> threshold
Nonagricultural pesticide use		17.56	21.95		limit value (TLV) ha
Agricultural pesticide use	0	2.83	16.02		been established for
Control instrument use	16.54	0	107.5		mercury in workroom
Tubes, switches use	7.53	0	46.26		air.
Lamp use	6.07	0	37.31		
Laboratory usage	2.28	5.92	1.59		
Consumer goods consumption:					
Pharmaceuticals		17.77	2.09		Food and Drug Adminis-
Paint	173.61	0	9.14		tration has estab-
Batteries	69.71	0	403.3		lished a limit for
Dental applications	0.93	16.65	. 0		mercury in edible fish of 0.5 mg/kg.
TOTALS	471.26	87.7	966.11		

Based on the data presented in this report, the following information needs to be obtained in future studies:

- Potential population exposed to mercury compounds from sources shown in Table 1.
- Concentrations of mercury in air, water, and land caused by anthropogenic sources.
- Efficiencies and costs of control technology for mercury pollutants.

It is recommended that further pollution assessment studies be implemented concerning copper smelting, coal combustion and paint manufacture and use since these operations contribute approximately 51% of the total mercury emitted from all known man-made sources. Approximately 85% of the total mercury lost to land areas results from copper smelting, chloralkali operations, and consumption of batteries, control instruments and tubes. The ultimate fate of this mercury is unknown and therefore requires further study.

#### SECTION 3

#### SOURCE DESCRIPTION

Although mercury is mined and produced in the United States, most of it is imported for use. It has unique properties which make its use very important to industry and science. Production and use are discussed in this section along with various chemical processes and properties.

# PHYSICAL AND CHEMICAL PROPERTIES

Mercury is a heavy metal which is liquid at normal temperatures. Table 2 describes some of the physical and chemical properties of mercury and various mercury compounds (1).

#### PRODUCTION

Principal sources of mercury include primary production from domestic ore, secondary mercury production from scrap materials, and imports. Primary production of mercury in the United States totalled 59 metric tons in 1974. This was a 20% decrease in primary production from 1973 when production totalled 73 metric tons (2).

Table 3 shows mercury mining operations and their location in the United States (3).

Production of mercury from scrap materials was 267 metric tons in 1973, while imports of mercury metal accounted for 1,576 metric tons during the same year (3).

<sup>(1)</sup> Stokinger, H. E. The Metals (Excluding Lead). In: Industrial Hygiene and Toxicology, Chapter 27, D. W. Fassett and D. D. Irish, eds. Interscience Publishers, New York, New York, 1962. 1090-1104 pp.

<sup>(2)</sup> Non-Ferrous Metal Data 1974. American Bureau of Metal Statistics, Inc., New York, New York, 1975. 143 pp.

<sup>(3)</sup> VanHorn, W. Materials Balance and Technology Assessment of Mercury and Its Compounds on National and Regional Bases. EPA-560/3-75-007, U.S. Environmental Protection Agency, Washington, D.C., October 1975. 433 pp.

TABLE 2. PHYSICAL AND CHEMICAL PROPERTIES OF MERCURY AND SOME OF ITS COMPOUNDS (1)

Chemical	Chemical symbol	Atomic or molecular weight	Specific gravity	Melting point, °C	Boiling point, °C	Solubility (temperature, °C) <sup>d</sup>
Mercury	Нд	200.61	13.546	-38.87	356.58	Insoluble hot or cold water dilute, hydrochloric acid, hydrogen bromide, hydrogen iodide.
Mercuric oxide (montroy- dite)	ндО	216.61	11.14	Decomposes 500		52 mg/m <sup>3</sup> 395 mg/m <sup>3</sup> (100) Soluble acids Insoluble alcohol, ether, acetone, alkalies, ammonia
Mercuric sulfide (cinnabar)	ндѕ	232.68	8.10	Sublimes 583.5		l0 mg/m <sup>3</sup> (18) Soluble sodium sulfide, aqua regia Insoluble nitric acid, alcohol
Mercuric chloride	HgCl <sub>2</sub>	271.52	5.44	276	302	36 kg/m <sup>3</sup> (0) 69 kg/m <sup>3</sup> (20) 613 kg/m <sup>3</sup> (100) 330 kg/m <sup>3</sup> alcohol 250 kg/m <sup>3</sup> ether Soluble acetic acid, pyridine
Mercurous sulfate	Hg <sub>2</sub> SO <sub>4</sub>	497.29	7.56	Decomposes	Decomposes	600 $g/m^3$ 900 $g/m^3$ (100) Soluble sulfuric acid, nitric acid
Mercuric acetate	нg (С <sub>2</sub> н <sub>3</sub> О <sub>2</sub> ) <sub>2</sub>	318.7	3.27	Decomposes		250 kg/m³ (10) 1,000 kg/m³ (100) Soluble alcohol, acetic acid
Mercuric fulminate	Hg (NCO) 2	284.65	4.42	Explodes		Slightly soluble cold water Soluble hot water, alcohol, ammonium hydroxide
Dimethyl mercury	Hg (CH <sub>3</sub> ) <sub>2</sub>	230.68	3.069		96	Soluble alcohol, ether
Ethyl mercuric chloride	C <sub>2</sub> H <sub>5</sub> HgCl	265.13	3.482	193		Insoluble cold water Very soluble hot alcohol Slightly soluble ether
Phenyl mercuric acetate	С6Н5Н9О2С2Н3	336.75		149		Slightly soluble hot or cold water Soluble glacial acetic acid, benzene, alcohol

a<sub>Unless</sub> otherwise stated, solubility is in water at 25°C.

Note.—Blanks indicate data not available.

TABLE 3. PRODUCTION OF U.S. MERCURY MINES IN 1973

Mine	County/state	Estimated production metric tons/yr
New Almaden	Santa Clara, CA	·25
Guadalupe	Santa Clara, CA	
Chilino Valley	Marin, CA	3
Corona	Napa, CA	4
Oat Hill	Napa, CA	
Manhattan-One-Shot	Napa, CA	
Mount Jackson	Sonoma, CA	9
Culver-Baer	Sonoma, CA	
Abbott	Lake, CA	2
Cardero	Humboldt, NV	23
Ruja	Humboldt, NV	
Study Butte	Brewster, TX	6
Alice and Bessie	Kuskokwim, AK	2
TOTAL		74

Note.—Blanks indicate data not available.

# PROCESS DESCRIPTIONS

The primary mercury industry is very small in the United States. The ore of economic importance is cinnabar mercury sulfide. The typical smelter industry practice is to feed mined mercury ore directly into kilns for recovery of mercury by roasting. Ore flotation is practiced for the beneficiation of low-grade ores. Currently, most mercury is produced through a directly heated pyrometallurgical process. Mechanical furnaces or retorts are used to roast mercury-bearing materials (4). Mercury vapors resulting from the roasting operation are drawn off and condensed to yield metallic mercury.

The secondary mercury production industry consists of approximately 300 small facilities utilizing a variety of mercury-bearing wastes as raw material sources. Wastes used in secondary processing include spent catalysts, batteries and industrial controls. Mercury from these sources is distilled off and condensed to form the product.

In both processes, two or three distillations are sometimes applied to give various degrees of mercury purity.

## **USES**

Of the total 1975 domestic mercury consumption of 1,964 metric tons, about 70% was from imports. New domestic capacity should reduce imports to about 50%. Secondary smelting currently accounts for 61% of domestic capacity. In 1973, consumption was 1,871 metric tons, as shown in Figure 1 (3).

Individual markets for mercury consumption are listed in Figure 1. Of these electrical apparatus manufacturing, electrolytic preparation of chlorine, and caustic soda account for 50% of the total mercury consumed in 1973. The cytotoxic properties of mercury compounds have given them a widespread usage as germicides and pesticides added to pharmaceuticals, plastics, paints, and other products. Methyl mercury and ethyl mercury have been banned for use in seed treatment due to their high toxicity. Methoxyethyl mercury (MEM) compounds have replaced the alkylmercury compounds in seed treatment. Phenylmercury acetate (PMA) has been extensively used as a fungicide and algaecide in paints, plastics, and other products. Under the conditions in which they are used, both types of compounds, PMA and MEM, are unstable and slowly release inorganic mercury. Table 4 presents a listing of 41 other mercury compounds produced by 13 companies.

<sup>(4)</sup> Kirk-Othmer Encyclopedia of Chemical Technology, Second Edition, Volume 13. John Wiley & Sons, Inc., New York, New York, 1967. 218-235 pp.

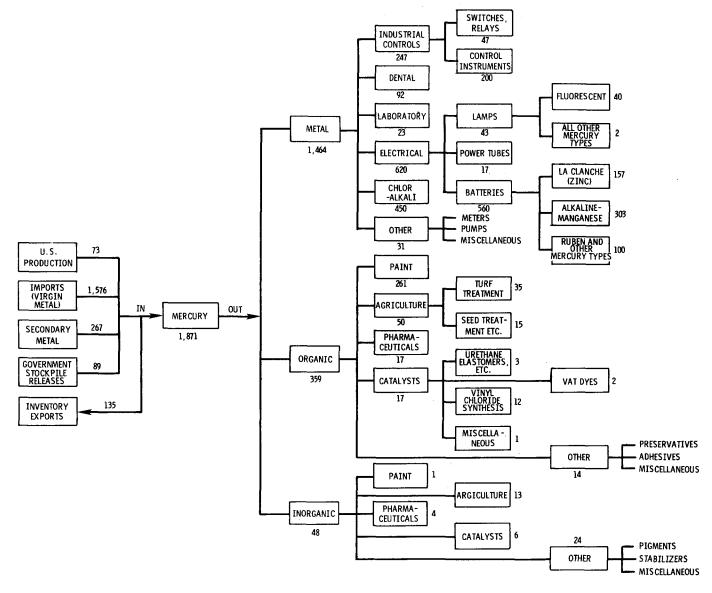


Figure 1. Sources of mercury and industrial and commercial usage in the United States, 1973 (metric tons/yr) (3).

TABLE 4. PRODUCERS OF MERCURY COMPOUNDS

Chemical	Company	Location
Di(phenylmercury) dodecenyl succinate	Tenneco Chemicals, Inc.	Elizabeth, NJ
Chloromethoxypropylmercuric acetate	Troy Chemical Corp.	Newark, NJ
Merbromin	Becton, Dickinson, Inc.	Baltimore, MD
Mercurial turf fungicides	Mallinckrodt, Inc./Industrial Chemicals	St. Louis, MO
Mercuric salicylate	Mallinckrodt, Inc./Drug and Cosmetic Chemicals Merck & Co., Inc./Chemical Manufacturing Division	St. Louis, MO Hawthorne, NJ
Mercurous chloride	Mallinckrodt, Inc./Industrial Chemicals	St. Louis, MO
Mercury ammoniated	Mallinckrodt, Inc./Drug and Cosmetic Chemicals	Jersey City,
Mercury bichloride	Mallincrodt, Inc./Industrial Chemicals  Merck & Co. Inc./Chemical Manufacturing Division Troy Chemical Corp	Jersey City, St. Louis, MO Hawthorne, NJ Newark, NJ
Mercury bromate	City Chemical Corp.	Jersey City,
Mercury bromide	City Chemical Corp. Merck & Co., Inc./Chemical Manufacturing Division	Jersey City, Hawthorne, NJ
Mercury chloride (mercurous)	Mallinckrodt, Inc./Industrial Chemicals Troy Chemical Corp.	Jersey City, St. Louis, MO Newark, NJ
Mercury cyanide	Mallinckrodt, Inc./Drug and Cosmetic Chemicals	Jersey City,
Mercury ethyl sulfate	City Chemical Corp.	Jersey City,
Mercury fluoride (mercuric)	City Chemical Corp. Pennwalt Corp./Ozark-Mahoning	Jersey City, Tulsa, OK
Mercury fluoride (mercurous)	City Chemical Corp.	Jersey City,
		(aontinu

(continued)

TABLE 4 (continued)

Chemical	Company	Location
Mercury iodate	City Chemical Corp.	Jersey City, NJ
Mercury iodide (mercuric)	Mallinckrodt, Inc./Drug and Cosmetic Chemicals	Jersey City, NJ
Mercury lactate	City Chemical Corp.	Jersey City, NJ
Mercury naphthenate	Troy Chemical Corp.	Newark, NJ
Mercury nitrate (mercuric)	City Chemical Corp. Mallinckrodt, Inc./Industrial Chemicals	Jersey City, NJ Jersey City, NJ
Mercury oxalate (mercuric)	City Chemical Corp.	Jersey City, NJ
Mercury oxalate (mercurous)	City Chemical Corp.	Jersey City, NJ
Mercury oxide, red	Mallinckrodt, Inc./Industrial Chemicals Merck & Co., Inc./Chemical Manufacturing Division Troy Chemical Corp.	Jersey City, NJ Hawthorne, NJ Newark, NJ
Mercury oxide, yellow	Mallinckrodt, Inc./Industrial Chemicals Merck & Co., Inc./Chemical Manufacturing Division Troy Chemical Corp.	Jersey City, NJ Hawthorne, NJ Newark, NJ
Mercury oxyfluoride	City Chemical Corp.	Jersey City, NJ
Mercury phosphate	City Chemical Corp.	Jersey City, NJ
Mercury stearate	City Chemical Corp.	Jersey City, NJ
Mercury succinate	City Chemical Corp.	Jersey City, NJ
Mercury succinimide	City Chemical Corp.	Jersey City, NJ
Mercury sulfate (mercuric sulfate)	Mallinckrodt, Inc./Industrial Chemicals Division Merck & Co., Inc./Merck Chemical Manufacturing Division G. Frederick Smith Chemical Co.	Jersey City, NJ Hawthorne, NJ Columbus, OH

(continued)

# TABLE 4 (continued)

Chemical	Company	Location
Mercury sulfocyanide (Mercuric sulfocyanide) (Mercury thiocyanate) (Mercuric thiocyanate)	R.S.A. Corp.	Ardsley, NY
Methylmercuric chloride	Strem Chemicals, Inc.	Danvers, MA
<pre>2-(Phenylmercuriamino)   ethyl acetate</pre>	W. A. Cleary Corp.	Somerset, NJ
Phenylmercuric acetate (PMA)	W. A. Cleary Corp. Cosan Chemical Co. Merck & Co., Inc./Chemical Manufacturing Division Tenneco Chemicals, Inc. Troy Chemical Corp.	Somerset, NJ Clifton, NJ Hawthorne, NJ Elizabeth, NJ Newark, NJ
Phenylmercuric ammonium acetate (PMAA)	Troy Chemical Corp.	Newark, NJ
Phenylmerciric lactate	Troy Chemical Corp.	Newark, NJ
Phenylmercuric oleate	W. A. Cleary Corp. Cosan Chemical Co. Merck & Co., Inc./Chemical Manufacturing Division Tenneco Chemicals, Inc. Troy Chemical Corp.	Somerset, NJ Clifton, NJ Hawthorne, NJ Elizabeth, NJ Newark, NJ
Phenylmercury borate	Cosan Chemical Co. Troy Chemical Corp.	Clifton, NJ Newark, NJ
Phenylmercury hydroxide	Merck & Co., Inc./Chemical Manufacturing Division	Hawthorne, NJ
Phenylmercury nitrate	Troy Chemical Corp.	Newark, NJ
Phenylmercury propionate	Merck & Co., Inc./Chemical Manufacturing Division	Hawthorne, NJ
Tolylmercuric chloride	Eastman Kodak/Organic Chemicals Division	Rochester, NY
Tris (2-hydroxyethyl) (phenylmercuric) ammonium lactate	W. A. Cleary Corp.	Somerset, NJ

#### SECTION 4

# ENVIRONMENTAL SIGNIFICANCE AND HEALTH EFFECTS

#### ENVIRONMENTAL SIGNIFICANCE

Mercury is circulated in the biosphere; approximately 1,200 metric tons are released annually to the atmosphere by degassing from the earth's crust and oceans (3). In nature, mainly in the aquatic environment, methyl mercury is produced from inorganic mercury by microbial activity.

Table 5 presents the sources and extent of mercury contamination in the environment. From this table, the source that accounts for 45% of the total mercury released (694 metric tons) is from final consumption of consumer goods. This includes consumer use of pharmaceuticals, paint, and batteries (3).

One source of environmental contamination by mercury is the burning of coal and petroleum. Analyses of fly ash from coalfired boilers show 10% or less of the original mercury remains from the coal. The major portion of mercury in coal is thus released to the air. Coal has been reported to contain between 0.012 parts per million (ppm) and 33 ppm of mercury.

The chloralkali industry is an example of a manufacturing process where mercury contamination is evident. Atmospheric emissions from the B. F. Goodrich plant in Calvert City, KY were reported to be 110 kg/day, far exceeding the National Air Emissions Standard of 1.3 kg/day. Of mercury losses, brine sludge represented about 60% of the total. Furthermore, a survey of Diamond Shamrock, Muscles Shoals, AL, showed that mercury losses were atmospheric emissions, principly from the mercury cell in chlorine manufacture. An investigation of mercury losses from Pennwalt in Calvert City, KY, revealed that most losses emanated from Emissions from these plants, however, cellroom ventilation. have been reduced due to the use of control technology. Water contamination from the chloralkali industry, once a dominant source, also has been greatly reduced through improved wastewater treatment.

In the primary lead industry, the major air emission is hot mercury-laden gas from the furnace. A typical condenser stack gas emission factor of 0.12 kg Hg per metric ton of lead ore processed has been reported. The concentration in the gas is

TABLE 5. TOTAL MERCURY LOSSES IN 1971 FOR THE UNITED STATES BY SECTOR AND SIC CATEGORY (3) (metric tons)

	Tota	l losses	to	Total mercury	Total
Source	Air	Water	Land	lost	recycled
Mercury mining and smelting:					
Mercury mining	0.01	0.00	0.01	0.02	0.00
Mercury processing	3732			3.02	
(including secondary)	7.84	0.00	0.41	8.25	0.00
Subtotals	7.85	0.00	0.42	8.27	0.00
	(1.7%)	(0.0%)	(0.0%)	(0.5%)	(0.0%)
Other mining:					
Copper mining	0.02	0.01	0.08	0.11	0.00
Zinc and lead mining	0.00	0.00	0.01	0.01	0.00
Copper smelting	40.77	2.26	2.26	45.29	0.00
Zinc smelting	4.59	0.25	0.25	5.09	0.00
Cement processing	0.50	0.25	1.76	2.51	0.00
Lime processing	0.08	0.04	0.29	0.41	0.00
Lead smelting	4.75	0.26	0.26	5.27	0.00
Subtotals	50.71	3.07	4.91	58.69	0.00
	(10.8%)	(3.5%)	(0.5%)	(3.8%)	(0.0%)
Unregulated sources:					
Livestock	0.00	0.0	17.70	17.70	0.00
Fuel oilresidential, commercial,					
and industrial	16.94	0.00	0.02	16.96	0.00
Refineries	1.15	0.00	1.15	2.30	0.00
Tars and asphalt	1.10	1.67	14.99	17.76	0.00
Coke ovens	7.16	0.51	2.56	10.23	0.00
CoalResidential, commercial, and				• • • •	
industrial	9.97	0.00	1.11	11.08	0.00
Utilitiesoil and natural gas	11.99	0.00	0.01	12.00	0.00
				1.	continued

(continued)

TABLE 5 (continued)

				Total	
		l losses		mercury	Total
Source	Air	Water	Land	lost	recycled
Unregulated sourcescontinued					
Natural gasresidential, commer-					
cial, and industrial	15.46	0.00	0.01	15.47	0.00
Utilitiescoal	40.71	0.00	4.52	45.23	0.00
Subtotals	104.48	2.18	42.07	148.73	0.00
	(22.2%)	(2.5%)	(4.4%)	(9.8%)	(0.00%
Manufacturing and processing:					
Caustic	0.00	7.61	1.90	9.51	0.00
Catalyst manufacture	0.00	0.02	0.00	0.02	0.00
Paint manufacture	0.01	0.20	0.05	0.26	0.00
Pesticide manufacture	0.00	0.06	0.00	0.06	0.00
Pharmaceuticals manufacture	0.00	0.02	0.00	0.02	0.00
Chloralkali	14.84	2.93	226.83	244.60	0.00
Textiles	0.00	0.15	7.63	7.78	0.00
Paint formulation	0.29	0.35	0.00	0.64	0.00
Control instrument manufacture	0.00	0.00	1.97	1.97	1.97
Catalyst usage	0.05	0.10	18.85	19.00	0.00
Other	10.28	10.23	8.70	29.21	20.66
Tubes/switches manufacture	0.00	0.00	1.57	1.57	0.00
Lamp manufacture	0.40	0.00	1.34	1.74	0.00
Battery manufacture	<u>0.1</u> 3	<u>0.0</u> 5	2.49	2.67	0.00
Subtotals	26.00	21.72	271.33	319.05	20.66
	(5.5%)	(24.8%)	(28.1%)	(21.0%)	(14.1%)
Final consumption:					
Commercial and industrial:					
Urethane and miscellaneous	0.12	0.00	2.22	2.34	0.00
Nonagricultural pesticide use	4.39	17.56	21.95	43.90	0.00
Agricultural pesticide use	0.00	2.83	16.02	18.85	0.00
<b>J</b>	2	•			.ontinuod

(continued)

TABLE 5 (continued)

				Total	
		l losses		mercury	Total
Source	Air	Water	Land	lost	recycled
Commercial and industrialcontinued					
Control instrument consumption	16.54	0.00	107.50	124.04	82.69
Tubes/switches consumption	7.53	0.00	46.26	53.79	0.00
Lamp consumption	6.07	0.00	37.31	43.38	0.00
Laboratory usage	2.28	5.92	1.59	9.79	12.98
Subtotals	36.93	26.31	232.85	296.09	95.67
	(7.8%)	(30.0%)	(24.1%)	(19.4%)	(65.2%)
Consumer goods:					
Pharmaceuticals consumption	1.04	17.77	2.00	20.90	0.00
Paint consumption	173.61	0.00	9.14	182.75	0.00
Battery consumption	69.71	0.00	403.30	473.01	24.89
Dental applications	0.93	16.65	0.00	17.58	5.55
Subtotals	245.29	34.42	414.53	694.24	30.44
	(52.0%)	(39.2%)	(42.9%)	(45.5%)	(20.7%)
TOTAL	471.26	87.70	966.11	1,525.07	146.77
Final disposal:					
Sewage	4.01	19.92	22.88	46.80	
Urban runoff	0.00	11.70	0.00	11.70	
Natural sources:					
	,018.70	0.00	0.00	1,018.70	
Runoff and groundwater	0.00	188.30	0.00	188.30	

7.86  $mg/mg^3$ . The amount of mercury discharged to wastewaters from primary lead production is insignificant.

The largest source of solid waste is the furnace or retort residue, amounting to some 207 kg/kg of metallic mercury produced. This calcined waste can vary widely in mercury content, with an estimated average of 100 ppm and 250 ppm for retorts and furnaces, respectively. These furnace residues together with mine rock and tailings are judged to have potential impacts on the environment.

The secondary mercury production industry consists of approximately 300 small facilities utilizing a variety of mercury-bearing wastes as raw material sources. An evaluation of the industry indicates that the estimated atmospheric mercury emissions are 2 kg/100 kg Hg processed. This amounts to 5.3 metric tons/yr of mercury emitted from the 267 metric tons produced annually by secondary processing.

#### HEALTH EFFECTS

Human exposure to mercury may occur in its mining and recovery or in any industry where mercury is being used. Mercury enters the body through the skin, gastrointestinal tract, or respiratory tract (4). Early symptoms of mercury poisoning include general weakness, exhaustion, mouth inflamation, loosening of teeth, excessive salivation, emotional instability, and body tremors (4). Chronic poisoning can develop rapidly and without warning.

Various mercury compounds differ in their toxicity to man. Mercuric salts have a fatal oral dose in man of 20 mg to 3 g (5). Alkyl mercury compounds exhibit high toxicity in man, causing death from injestion of several milligrams (5).

<sup>(5)</sup> Quality Criteria for Water. EPA-440/9-76-023, U.S. Environmental Protection Agency, Washington, D.C., October 1975. 501 pp.

#### SECTION 5

# CONTROL TECHNOLOGY

In the primary smelting industry, attention is focused on air emissions control. Mist eliminators and wet-scrubbers are the major control devices. Available data indicate that 50% to 70% of the mercury emitted from the stacks of primary extraction facilities is particulate. In the secondary production industry, emission controls include direct and indirect condensation, chemical scrubbing, and adsorption.

In an experimental study of a chloralkai plants, wastewater ranged from 3 ppm to 18 ppm mercury, while brine sludge was 150 ppm to 1,500 ppm mercury. The most effective control techniques were sulfide precipitation for the water treatment and high temperature roasting for the treatment of sludge. Effluent mercury levels ranged from 10 parts per billion (ppb) to 125 ppb, with an average removal efficiency of 96.8%.

# AIR EMISSIONS

Various processes have been developed for removing mercury vapor from air and other gases (6). One process achieves mercury removal from gases by impregnating materials (including metal such as gold, silver, cadmium, indium, thallium, aluminum, lead, gallium, and copper) on activated carbon. These products will rapidly and quantitatively remove mercury vapor from air as well as from other gases, including hydrogen, carbon dioxide, nitrogen, and oxygen. The high surface area of the activated carbon, which is impregnated with the mercury reactant, appears to be partially responsible for the greatly improved adsorption of the mercury vapor; the carbon appears to activate the metal thus enabling the mercury to be adsorbed by the impregnating material (metal).

Another process involves removing mercury from a gas stream by washing the gas with alkaline hypochlorite containing added alkali metal or calcium chloride. The alkaline hypochlorite solution can be sodium hypochlorite. Sodium hypochlorite solutions are well known in commerce and normally contain sodium hypochlorite and sodium chloride of approximately equimolar proportions. When mercury vapor is reacted with such solutions or

<sup>(6)</sup> Sittig, M. Pollutant Handbook. Noyes Data Corporation, Park Ridge, New Jersey, 1973. 286-308 pp.

with solutions prepared by diluting the commercial solutions with water, a precipitate of insoluble mercury compounds is formed. This is inconvenient because it tends to settle out in vessels and pipelines and the like and makes the recovery of the mercury more difficult. It has been discovered, however, that if additional alkali metal chloride or calcium chloride is added to the alkaline hypochlorite solution, the mercury remains in solution, possibly in the form of a complex anion. The amount of additional sodium or calcium chloride to prevent mercury compounds precipitating depends upon the composition of the solution, particularly with respect to pH.

Washing the mercury-containing gas streams may be carried out in any gas-liquid contacting device; for example, a column packed with Raschig rings or on diffuser plates. It may be carried out in ambient temperature or at any other convenient temperature. Mercury may then be recovered from the solution either chemically or electrolytically. A suitable electrolytic cell for recovering the mercury contains a graphite or platinized titanium anode and a mercury cathode. The mercury in solution is reduced at the cathode. A preferred method of recovering mercury from the absorbing solution is to blend it slowly into the feed brine stream supplying one or more commercial mercury cells. The mercury in solution is then recovered electrolytically at the cathode.

# WASTEWATER EFFLUENTS

A variety of processes for mercury removal from water have similarly been developed (6). One process involves recovering mercury from brine effluent from mercury cathode electrolytic cells. The mercury cathode electrolytic cells are constructed with a relatively small gap between a fixed anode and a steel plate or other current-conducting material. In the operation of these cells, saturated sodium chloride or potassium chloride brine and mercury are passed through this gap during the electrolysis. The mercury upon entering the cell spreads over the steel plate or other conducting material and acts as a cathode for the cell.

In the process, saturated brine solutions are used. After passing the brine once through the cell, the brine discharged from the cell is dechlorinated by air stripping or other means, resaturated, and recycled again through the cell. In passing through the cell, the chloride concentration of the brine is seldom reduced over 20%. Thus, the brine discharge from the cell is still relatively saturated.

While mercury cathode cells have many advantages over other conventional cells, a small but significant amount of mercury is lost in the process. A major portion of the mercury loss results from the chlorination of the mercury to a soluble salt which dissolves in the brine as it passes through the cell. This mercury

which reacts with the chlorinated brine is often lost in the resaturation step of the process. Thus, the brine leaving the cell may contain as much as 50 parts of mercury per million parts of brine.

An aqueous solution having a pH between 2 and 11 and containing from 1 ppm to 500 ppm of dissolved mercury can be cleaved with a reducing agent. This is done by bringing a substantially waterstable solid metallic reducing agent having a greater solution potential than mercury into contact with the solution; elemental metallic mercury is liberated. The liberated mercury amalgamates the surfaces of the reducing agent and also coalesces into droplets on the surfaces.

Depending on the manner of carrying out the process, particles of amalgam and mercury droplets are either allowed to fall from the reducing agent and collected from time to time, or the amalgam and mercury droplets are flushed from the surfaces of the reducing agent along with inert solid formed and recovered from the flushing liquid by settling or filtration. Impure mercury recovered in this manner is purified by standard methods, such as acid washing or retorting or by a combination of methods. If desired, mercury may also be recovered by removing the reducing agent from the reaction zone periodically along with accumulated reaction products and by retorting the entire mass.

### SLUDGES

A number of processes have also been developed for removal of mercury from sediments and sludges (6). For example, one process involves recovering mercury from sludge from a purification tank for the purification of saturated alkali chloride solution obtained in the production of caustic alkali and chlorine by the electrolysis of alkali chloride solution in the so-called "mercury process."

In the electrolysis of alkali chloride solution by the mercury process, alkali chloride is usually dissolved in water to a concentration of about 0.3 g/m³ and this saturated alkali chloride solution is introduced into an electrolytic cell fitted with a mercury cathode. The electrolysis is then carried out, and sodium amalgam is produced at the mercury cathode, while chlorine gas is generated at the anode and subsequently collected. According to the above electrolytic step, about 10% of the alkali chloride in the influent alkali chloride solution is electrolyzed after which it is exhausted from the electrolytic cell.

Additional alkali chloride is dissolved in this depleted brine to produce again the saturated alkali chloride solution. The saturated alkali chloride solution, from which impurities such as calcium, magnesium, and sulfate mixed together with the

additional alkali chloride are removed in a purification step, is again circulated into the electrolytic cell.

The efficiencies of the control methods described for mercury removal from air, water and solids are not known. The extent to which these control techniques are applicable to specific industries where mercury is present as a pollutant is unknown.

# SECTION 6

# REGULATORY ACTION IN PROGRESS

Past regulations established by EPA concerning mercury are cited in Table 6 (3). The FDA has established a guideline for mercury in edible fish of 0.5 mg/kg (5). The American Conference of Governmental Industrial Hygienists has established a threshold limit value (TLV) of 0.05 mg/m $^3$  for mercury in workroom air (7).

Mercury has been designated as a priority pollutant for study under the Federal Water Pollution Control Act. Best available technology and pretreatment primary standards are to be reviewed in the near future.

<sup>(7)</sup> TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1976. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1976. 94 pp.

TABLE 6. EPA MERCURY REGULATIONS (3)<sup>a</sup>

Federal Register	Date	Applicable to	Standard
38 FR 8820 <sup>b</sup>	4/06/73	Mercury ore processing facilities and chloralkali plants.	2.3 kg/24-hr period
38 FR 35388 (proposed)	12/27/73	Paper and allied products, oil and gas extraction, industrial organic or inorganic chemical,	Streams, lakes, or estuaries with flow <0.28 m <sup>3</sup> /s or lakes <2.02 km <sup>2</sup> no discharges.
(39 FR 10603		Other streams and lakes20 mg/m <sup>3</sup> /discharge or 1/10th this concentration when low flow is <10 times the waste flow.	
bituminous coal and lignite mining, storage or primary battery manufacturing, or metal mining facility discharging	Other estuaries and all coastal waters 100 mg/m <sup>3</sup> /discharge or 1/10th this concentration where low flow is <10 times the waste flow.		
	into navigable water.	Streamnot to exceed 0.005786 times flow in m <sup>3</sup> /s or 0.73 kg/day.	
			Lakenot to exceed 0.004821 times flow in m <sup>3</sup> /s or 0.61 kg/day.
			Estuarynot to exceed 0.00027 times flow in $m^3/s$ or 1.22 kg/day.
			Coastal waternot to exceed 0.009642 times flow in $m^3/s$ or 1.47 kg/day.
38 FR 28610	10/15/73	Ocean dumping.	No mercury except as trace contaminants.
39 FR 38064	10/25/74	Wastewater treatment plant sludge incinerators.	3.2 kg/24-hr period.

This table does not include regulations dealing with mercury-based pesticides. There have been and continue to be many such regulations, all involving either cancellation or suspension of pesticide use.

b Federal Register, 38:3820.

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- 7. TLVs® Threshold Limit Values for Chemical Substances and Physical Agents in the Workroom Environment with Intended Changes for 1975. American Conference of Governmental Industrial Hygienists, Cincinnati, Ohio, 1975. 94 pp.

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# 16. ABSTRACT

This report lists the properties, production sources, amounts, and uses of mercury. Mercury pollution figures, sources, health effects, environmental significance, and control technologies are cited. Areas are listed where information is lacking or further study is required.

17. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS	b.IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group			
mercury, metals, transition metals, cinna- bar, mercury isotopes, mercury alloys, mercury amalgrams, mercury halides,	smelting, mercury ore refining, chloralkali plants	68D 68G			
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