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TRENDS IN USAGE OF MERCURY

# REPORT

# of the

PANEL ON MERCURY

COMMITTEE ON TECHNICAL ASPECTS OF CRITICAL & STRATEGIC MATERIALS

# NATIONAL MATERIALS ADVISORY BOARD

DIVISION OF ENGINEERING-NATIONAL RESEARCH COUNCIL

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#### TRENDS IN USAGE OF MERCURY

#### INTRODUCTION

Mercury has been used by mankind since prehistoric times. As a metal, it possesses an unusual combination of useful properties which include:

- liquidity at ordinary temperatures
- high surface tension
- uniform volume expansion
- good electrical conductivity
- an ability to alloy readily
- high density
- chemical stability
- toxicity of its compounds

Until the 16th century, the consumption of mercury was small and chiefly in medicine. Since then, mercury's applications have paralleled scientific advancements and current principal uses of mercury in the United States are in electrical apparatus, the electrolytic preparation of chlorine and caustic soda, paints, industrial and control instruments, pharmaceuticals, and agriculture. Other materials may be substituted for mercury in some applications. However, for those uses which require mercury's unusual combination of chemical and physical properties, there is no ideal substitute.

This report assesses the present and projected uses for mercury over the next five to seven-year period.

#### RAW MATERIALS AVAILABILITY

#### Natural Occurrence & Reserves

Of 25 minerals known to contain mercury, the chief source is the red sulfide, cinnabar (HgS). Important deposits are located in the United States, China, Italy, Mexico, the Phillippines, Peru, Spain, the U.S.S.R., and Yugoslavia.

In 1959, the measured, indicated, and inferred world reserves<sup>(a)</sup> of mercury ore were estimated as 4 million flasks<sup>(b)</sup>, with the United States accounting for about 300,000 flasks<sup>(1)\*</sup>. The U.S. Department of Interior has been keenly aware of the demand-supply situation for mercury and its ores. Thus, in 1965, the Bureau of Mines published the results of an extensive survey of the domestic resources of mercury producible at various price ranges for each mine<sup>(2)</sup>: This included an estimate of the available nationwide production potential based on a study of past price and production relationships. Among the conclusions offered in this report were the following:

- (1) Existing U.S. resources were estimated as 1,465,000 flasks, although much of this is in low-grade material.
- (2) A total yearly production of 60,000 flasks would be required to make the U.S. self-sufficient in mercury at present (i.e., 1964) rates of consumption. This production could be maintained for 10 or more years from existing resources producible at a price of \$500 (constant dollars, 1957-59 = 100)\*\* per flask.
- (a) Minable at about \$250 a flask.
- (b) The unit of marketing in the mercury industry is a steel flask containing 76 pounds of mercury.
- (\*) References cited are listed at the end of this report.
- (\*\*) Quoted price divided by Bureau of Labor Statistics Wholesale
  price index (1957-1959) = 100.

(3) Enough mercury resources producible at \$1,000 per flask exist, along with expected new discoveries, to allow production of a 60,000-flask-per-year rate for many more decades.

Previously, a 1964 Geological Survey report<sup>(3)</sup>identified various factors responsible for the gap between domestic production and consumption and cautioned against expecting a quick response in domestic production even though the price for mercury has become increasingly more favorable. This advice appears well given, particularly in view of the fact that - as noted below - the domestic production of mercury has not risen above the level of 24,000 flasks over the past four years even though the average price per flask has ranged from \$440 to \$571 over this time period.

# Domestic Production and Reclamation

#### Primary Sources

Trends in the production, consumption, and price of mercury over the period of 1945-1968 are shown in Figure 1. As indicated, the domestic primary production of mercury in the United States during 1968 continued to rise, for the fourth consecutive year, to 24,975 flasks. During 1968, mercury was produced in Alaska, Arizona, California, Idaho, Nevada, Oregon, Texas, and Washington, with California and Nevada accounting for 90 percent of the total. Table 1 describes the ore treated and mercury produced over the period, 1961-1967 inclusive.

The estimated average U.S. price was \$535.56 for 1968, compared with average prices of \$489.36 in 1967 and of \$341.58 for the 5-year period, 1962-1966.

#### Secondary Sources

Production of secondary mercury rose to 33,405 flasks in 1968. As shown in Table 2, this was the highest level of secondary mercury

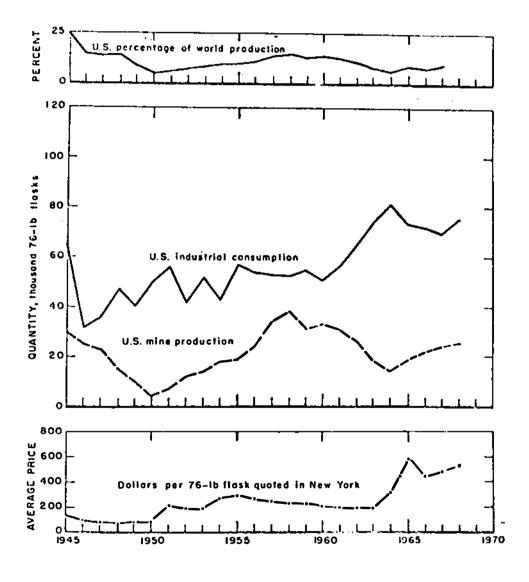


FIGURE 1. TRENDS IN PRODUCTION, CONSUMPTION, AND PRICE OF MERCURY (4,5)

		Mei	ccury Produced
	Ore Treated,		Pounds per Ton
Year	short tons	Flasks	of Ore
1961	262,108	31,633	9.2
1962	146,523	26,228	13,6
1963	113,539	19,101	12.8
1964	149,907	14,115	7.2
1965	339,124	19,353	4.3
1966	321,080	21,993	5.2
1967	439,753	23,767	4.1

TABLE 1.MERCURY ORE TREATED AND MERCURY<br/>PRODUCED IN THE UNITED STATES(a)(4)

(a) Excludes mercury produced from placer operations and from clean-up at furnaces and other plants.

	UNITED STATES
Year	Flasks(a)
1961	8,360
1962	5,800
1963	10,520
1964	24,519
1965	46,670
1966	16,400
1967	22,150
1968	33,405

TABLE 2. PRODUCTION OF SECONDARY MERCURY IN THE UNITED STATES<sup>(4,5,6)</sup>

(a) Includes GSA releases.

production since 1965 in which year the total was swelled by an AEC release of 29,753 flasks.

The 1968 statistics for secondary mercury production include a total of 19,610 flasks which represent sales by GSA. Other sources of secondary mercury were battery scrap, reclaimed dental amalgams, and sludges.

#### Refining

With the gradual depletion of the higher-grade ores, concentration of lower-grade ores prior to roasting or leaching is assuming more importance. Methods of beneficiating mercury ore include hand sorting, crushing, screening, jigging, tabling, and flotation. Of these methods, flotation is the most efficient and produces 25 to 50 percent concentrates with mercury recoveries of about 90 percent.

Roasting is the conventional process used for extracting mercury from its ores and concentrates. It is essentially a distillation process in which the ore is heated in a mechanical furnace or retort to vaporize the mercury, followed by cooling and condensation of the vapor to liquid metal. Recovery of mercury is high, averaging about 95 percent for furnace plants and 98 percent for retort installations. In addition, the product, prime or virgin mercury, averages about 99.9 percent pure which is satisfactory for virtually all uses.

#### Legislation and Government Programs

Through the Office of Mineral Exploration (OME) of the Geological Survey, the Federal Government has offered financial aid to qualified applicants searching for mercury. The offering of 50 percent of total allowable exploration costs at eligible domestic mercury deposits, in effect since 1957, was raised in September of 1967 to 75 percent. This level of support still continues.

The stockpile objectives for mercury, which had been changed during 1966 to 200,000 flasks for conventional war and 8,600 flasks for nuclear war, remained the same in 1968. As of September 30, 1968, there were 200,266 flasks in the stockpile, Of this, 200,000 flasks were of stockpile grade, i.e., of not less than 99.9 percent chemical purity.

Total releases of surplus mercury by GSA during 1968 were 19,610 flasks leaving a surplus of only about 2,000 flasks at the year's end. This stock is expected to be exhausted in early 1969 and came from stocks previously transferred to GSA by the Atomic Energy Commission (AEC). In 1965, the AEC had offered 38,000 flasks to GSA but withdrew the offer in 1966 and instead offered 20,000 flasks.

#### Imports

As shown in Table 3, imports of mercury in 1968 totaled 23,953 flasks. It is of some interest to note that a substantial portion of the 1968 imports came from the new COMINCO mine in Canada which went into operation only last fall.

#### USE PATTERN

#### Bureau of Mines Statistics

For many years, the U.S. Bureau of Mines has grouped the principal uses of mercury according to the categories shown in Table 4. Accordingly, this breakdown and the accompanying statistics for the period of 1961-1968 serve as a logical reference point in reviewing present and future trends in the usage of mercury.

It may be noted that these statistics, specifically those for the use categories of electrical apparatus, mildew proofing paints, and pharmaceuticals, were recently revised to correct reporting errors for which the Bureau of Mines was not responsible.

TABLE 3. U.S. GENERAL IMPORTS<sup>(a)</sup> OF MERCURY BY COUNTRIES<sup>(4,5)</sup>

		Import	s, flasks	
Continent & Country	1965	1966	1967	1968
North America:				
Canada	32	349	391	5,625
Mexico	1,825	7,049	1,260	2,339
South America:	_,	.,	_,	-,
Argentina				142
Bolivia	50		40	20
Chile				40
Peru	1,899	741	1,037	1,160
Other:	•		•	•
France			250	
Germany, West	150			
Italy	1,297	14,485	5,117	351
Japan		50		
Netherlands			200	
Philippines		1,150	550	
Spain	10,996	7,656	11,969	12,899
Sweden				6
Turkey	135			
United Kingdom	3	<b>(</b> b)		
Yugoslavia	1,415	3,277	3,085	1,371
Total	s 17,838	34,757	23,899	23,953

(a) Data are "general" imports; that is, they include mercury imported for immediate consumption plus material entering the country under bond.

(b) Less than 1/2 flask.

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	Consumption, flasks							
Use	1961	1962	<u>1963</u>	1964	1965	1966	<u>1</u> 967	1968(c
Agriculture (includes fungicides and bactericides								
for industrial purposes)	2,557	4,266	2,538	3,144	3,116	2,374	3,732	3,430
Amalgamation	278	299	306	308	268	248	219	259
Catalysts	707	874	612	656	924	1,932	2,489	1,743
Latalysts (a) Dental preparations (a)	2,154	2,033	2,346	2,612	1,619	1,334	1,359	2,089
Electrical apparatus <sup>(a)</sup>	10,255	11,564	11,115	10,690	13,931	13,339	13,823	19,166 <sup>(d)</sup>
Electrolytic preparation of chlorine & caustic soda	6,056	7,314	7,999	9,572	8,753	11,541	14,306	17,424
General laboratory use:	-		•	-				
Commercial	1,484	1,752	1,241	1,583	1,119	1,563	1,133	1,202
Government			3,821	15,746				
Industrial & control instruments <sup>(a)</sup>	5,627	5,186	4,943	4,972	4,628	4,097	3,865	2,841
Paint:	-		•	•		•		
Antifouling	915	124	252	547	255	140	152	ን 8,611
Mildew proofing	5,146	4,554	6,403	4,898	7,534	7,762	6,151	J
Paper & pulp manufacture	3,094	2,600	2,831	2,148	619	612	446	417
Pharmaceutiçals	2,515	3,378	4,081	5,047	3,261	3,668	1,945	397(d)
Redistilled <sup>(a)</sup>	9,013	8,987	9,227	11,697	12,131	7,267	7,334	8,418
Redistilled <sup>(a)</sup> Other <sup>(b)</sup>	5,962	12,370	20,248	7,734	15,402	15,632	12,563	7,805
Totals	55,763	65 <b>,3</b> 01	77,963	81,354	73,560	71,509	69,517	76,030 <sup>(c)</sup>

TABLE 4. MERCURY CONSUMED IN THE UNITED STATES BY USES (4, 5, 7)

- (a) A breakdown of the "redistilled" classification showed averages of 43 percent for instruments, 14 percent for dental preparations, 23 percent for electrical apparatus, and 20 percent for all other uses in 1963-1966, compared with 49 percent for instruments, 14 percent for dental preparations, 22 percent for electrical apparatus, 11 percent for general laboratory, and 4 percent for all other uses in 1967.
- (b) For 1963-1967, "other" includes mercury used for installation and expansion of chlorine caustic soda plants and vermilion.
- (c) Individual values represent totals of quarterly periods. These items do not add to the grand total which has been increased to cover approximate total consumption.
- (d) Revised on the basis of private communications with the U.S. Bureau of Mines, March 20, 1969.

This Panel was also advised that the Bureau of Mines is currently in the process of revising the questionnaire used to collect statistical information on mercury. Among the anticipated changes are some which will lead to an elimination of the need for breakdowns in the applications for redistilled mercury. These efforts are fully endorsed by this Panel.

### Present and Future Trends

As shown in Table 4, the consumption of mercury continued at a high level in 1968. A breakdown and analysis of the trends in these use categories over the last 5-year period is of some interest and is given in Table 5.

As noted, about 2/3 of the total 1968 consumption was accounted for by four major use categories which have shown an increasing level of consumption over the past 5 years. Of these four uses, applications in electrical apparatus and the electrolytic preparation of chlorine and soda have dominated all others. Declining levels of consumption were indicated for industrial and control instruments, dental preparations, pharmaceuticals, and in paper and pulp manufacture.

Each of the major use categories was reviewed with the objective of assessing trends in consumption and possible substitutions over the next 5- to 7-year period. These assessments are presented in the sections which follow.

# Agriculture

The primary use of mercury in agriculture has been for seed treatment of cereal grains. Secondary uses are for disease control of fruits, vegetables, etc. Mercurial disease control usage has a long history of successful application with the added advantage of being relatively inexpensive. The major commercial applications are with generally mature products vulnerable to being supplanted by newer and/or more effective materials. Therefore, the opportunities for increased usage and new applications are either non-existent or severely limited.

		1968	Consumption
Use		Flasks	Percent of Total
Increas	ing Level of C	onsumption	
Electrical Apparatus <sup>(a)</sup> Electrolytic preparation of ch Paints	lorine & soda	21,018 17,424 8,611	28.5 23.6 11.7
Catalysts	Subtotal	$\frac{1,743}{48,796}$	$\frac{2.4}{66.2}$
<u>No Signifi</u>	cant Changes i	n Consumption	
Agriculture General Laboratory Use <sup>(a)</sup> Redistilled Amalgamation Other uses		3,430 2,128 337 259 <u>7,805</u>	4.7 2.9 0.5 0.3 <u>10,6</u> 19,0
Decreasi	Subtotal	13,959 nsumption	19.0
Industrial & Control Instrumen Pharmaceuticals Dental Preparations <sup>(a)</sup> Paper & Pulp Manufacture	uts <sup>(a)</sup> Subtotal	6,965 397 3,120 <u>417</u> 10,899	9.5 0.5 4.2 <u>0.6</u> 14.8
Gr	and Total	73,654 <sup>(b)</sup>	100.0

# TABLE 5. TRENDS IN USES OF MERCURY OVER THE PERIOD 1964-1968

(a) 1968 consumption in these categories was increased to include the quantity of redistilled mercury according to the 1967 percentile values given in Footnote (a) of Table 4.

(b) Total of four quarterly periods.

Yearly mercury consumption figures show a somewhat erratic picture, probably due to variable bid export business and/or reflection of its recent wide price fluctuation. The most reasonable current agricultural consumption estimate would be in the neighborhood of 3,000 flasks/year with a forecast decline of about 2 percent per year over the next 5 years, as indicated below.

Year	Flasks of Mercury Required
1968	3,430
1969	3,000
1970	2,940
1971	2,880
1972	2,820
1973	2,760

So far as possible substitutes are concerned, the critical area of agricultural mercury consumption is for seed treatments, notably cereal grains and cotton. There is not currently available, at any price, a product combining the broad spectrum control achieved by mercury compounds. A few specialty, high priced products are available which control disease in the same areas as the mercurials, but the gaps where no disease control is available are serious. Our best current estimate of the critical seed treatment mercury requirement is 1,200-1,500 flasks annually.

#### Amalgamation

Almost all metals can be amalgamated with mercury, the prominent exception being iron. Depending upon the metal and the amount being alloyed, the resulting mixture is either liquid or solid.

Mercury was widely used in the early days of gold mining to recover free gold and silver from placer and lode ores. These uses practically disappeared when the free-milling ores were depleted and when the cyanide process was developed.

Potassium, sodium, and zinc amalgams are used as reducing agents. Zinc amalgam is used in the reduction of  $\gamma$ -keto acids. Sodium amalgam has been used in production of tetraethyl lead. However, a continuous

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electrolytic process suitable for producing either tetraethyl lead or tetramethyl lead threatens to curtail further the use of sodium amalgam.

An electrolytic process for recovery of zinc from drosses or other by-products involves precipitation of elemental zinc at the cathode and alloying with mercury. The mercury forms a moving cathode, and as it is extracted from the electrolytic cell, it carries a small amount of zinc. The zinc is then deposited on an aluminum cathode and can be stripped electrolytically. Zinc of high purity is recovered. Amalgam metallurgy also has been tried for the recovery of aluminum, bismuth, cadmium, copper, indium, lead, manganese, nickel, sodium, tin, and thallium. None of these operations has proven economically attractive.

The pronounced success of mercury as an electrode in chlorine cells encouraged its use for similar purposes, particularly where a metal is released that will amalgamate sufficiently. Uranium and vanadium can be separated and recovered by such electrolysis of carbonate-leach solutions. Whether or not usable fuel can be so reclaimed from reactor cores is not known.

In general, amalgamation seems to be a dwindling market for mercury for ecomonic reasons as well as technological obsolescence. The consensus of this Panel is that these applications for mercury are likely to remain at a level of 200 to 250 flasks per year over the period through 1975.

#### Catalysts

Table 6 presents an estimation of anticipated demand for mercury's use as a catalyst between 1968 and 1975. The total shown for 1968 is a preliminary government figure; all other data are estimates made by persons in industry. Overall 1968 consumption is down nearly 800 flasks from 1967 usage of 2,489 flasks. Expected recovery in demand in 1975 will still be less than 1967 levels. In all cases, prime

virgin mercury is acceptable as the base material in preparing catalytic salts.

TABLE 6. ESTIMATED I CATALYST I		
	<u>No.</u>	f Flasks
	1968	1975
irethane	800	1,560
inyl Chloride Monomer	500	250
nthraquinone Derivatives	175	220
iscellaneous	236	340
	1,711	2,370

Owing to the ever-present threat of technological obsolescence, the 1975 projections must be viewed as probable guidelines only. Mercurybased catalysts have been replaced by other catalysts in the past, two examples being vinyl acetate monomer and acetaldehyde. It could happen again; or needs could increase, such as in urethane production.

Accepting the prior yearly totals at face value indicates an overall growth rate of 3.7 percent per year through 1975, motivated primarily by urethanes.

Organic mercurial salts are used in urethane elastomers for casting, sheeting and sealant applications, frequently as a replacement for stannous octoate catalysts. It is generally conceded that phenyl mercuric oleate and acetate are not used to make flexible urethane foams. One of the outstanding outlets in 1968 was the incorporation of organic mercury catalysts in a urethane resin, molded into a nearly indestructible automobile bumper on one series of an intermediate priced car. Considerably more should be consumed in 1969 as all series of this automobile, excepting one, incorporate this feature. No other car makers are known to be using this innovation on their vehicles.

Ordinarily, about three parts of the commercial mercury catalyst are employed in each 100 parts of resin. Active content of mercury in the catalyst is about 5 percent. A low cost sealant, in the multimillion pound range, also employs PMA (phenyl mercuric acetate) catalyst. In this case, about 0.1 percent of the PMA dissolved in a solvent is used for each 100 parts of resin. Active content of mercury in the catalyst is again 5 percent. Cellulosic sheeting is backed by these kinds of urethane elastomers and is the subject of U.S. and foreign patents.

Although the overall growth rate of the urethane business as a whole is 12 percent, a more conservative 10 percent has been used. A diversity of catalysts are available, such as the amines and a number of other metallic compounds. The amines and stannous soaps and salts are the most popular catalysts being used today and are considerably cheaper in price per pound than the mercurials.

Vinyl chloride monomer production has shown a strong shift toward the use of ethylene, a more inexpensive feedstock than acetylene. A number of acetylene-based plants were shut down in 1968, which will temporarily bring the ratio of demand versus production capacity into a better balance. Meanwhile, large new facilities based on ethylene are under construction. No new acetylene-based plants are visualized as being authorized because of unfavorable manufacturing costs versus ethylene. Conventionally about 0.074 pound of mercury used as mercuric chloride catalyst has been consumed per thousand pounds of vinyl chloride monomer in the acetylene process. Should the present acetylenebased plants remain in operation through 1975, the total mercury demand that year is expected to fluctuate somewhere between 200 and 300 flasks.

Sulfonated anthraquinone products are raw materials to make vat dyes. Mercury used in the form of a mercuric oxide catalyst is expected

to retain its place in the industry without rivalry from any replacement catalyst for the foreseeable future. Excluding 2-anthraquinone sulfonic acid, all other sulfonic acid derivatives reportedly require a mercury-based catalyst. Projections to 1975 are based on a trend line from 1958 and are equivalent to about  $2-\frac{1}{2}$  percent annual future growth.

Miscellaneous uses which accounted for over 200 flasks in 1968 include a broad spectrum of minor uses. The literature cites a lengthy list of mercury catalyst potentialities. In addition, work continues in new fields, such as reactions involving photochemistry, other sulfonation products, Ziegler syntheses, polymers, and manufacturing fluorine chemicals. Forecasting 1975 demand utilized expected non-durable production indices, approximating 5 percent annual growth.

#### Dental Applications

Mercury is used in an amalgam with a silver/tin alloy for the filling of teeth cavities. Its use in such fillings dates back to the turn of the century, and is well defined and well accepted. The attributes of this mercury/silver dental amalgam which have continued its use are: inertness; relative permanence; ease of handling by the dentist; compressive strength; and abrasion resistance.

The published Bureau of Mines statistics list two categories of mercury sales into dental applications. (1) Uses served by prime virgin mercury; and (2) Utilization of a fraction of the redistilled mercury production. Presumably, the total sales of mercury metal for dental applications would be the sum of these two items. These statistics are given below for the period 1961-1968.

#### Mercury Consumption, flasks

Year	<u>Ftam</u>	Redistilled	<u>Total</u>
1961	2,154	1,172	3,326
1962	2,033	1,258	3,291
1963	2,346	1,200	3,546
1964	2,612	2,395	5,007
1965	1,619	1,839	3,458
1966	1,334	775	2,109
1967	1,359	1,026	2,385
1968	2,089	1,238	3,327

Analysis of these data indicates years of relatively constant sales (1961, 1962, 1963, 1965 and 1968); a year with sharp increase (1964); and years of sharp declines (1966 and 1967). It is unlikely that the actual <u>consumption</u> of mercury in dental amalgams follows such a pattern. There can be two explanations: (1) the data reported are accurate, but represent unusual buying patterns resulting from price fluctuations or other external effects, (2) the consumption and sales are approximately equal and follow a relatively smooth growth pattern with reporting errors and omissions accounting for the fluctuations.

There is no indication that consumption of mercury in dental amalgam would have followed an erratic pattern. Analysis of the consumption of mercury, from the standpoint of both the mercury and the silver alloy involved, indicates that 1968 consumption was 3,500 flasks,  $\pm$  500 flasks per year. (This would make 1964, 1966, and 1967 data as reported to the Bureau of Mines incorrect.) The consumption of dental amalgam has, over the past 10 years, and probably will over the next 10 years, follow population patterns. Assuming the 3,500 flasks figure as a "most likely" number for 1968, 1958 would have been 3,000 flasks, and 1963 would have been 3,200 flasks, based on population statistics.

Population projections would indicate the growth of mercury in dental amalgams to approximately 3,800 flasks per year in 1975, with probable limits being 3,500 to 4,400 flasks in that year.

At the present time, under normal economic conditions, no substitutes have been able to displace the mercury/silver amalgam in dental restorations. However, in critical times, if mercury were in extremely short supply, its use in these dental amalgams could be sharply curtailed, to practically zero if necessary. Current substitutes, although not as permanent (they might require periodic replacement) could be used to produce satisfactory restorations. These substitutes would include silicate/zinc phosphate cements, or acrylate and epoxy resins. Since plastics technology progresses rapidly, it is not unlikely that under the pressure of curtailment of mercury supply, the quality of these substitutes could be improved dramatically.

# <u>Electrical Apparatus, Instruments, and Laboratory Uses</u>

This Panel identified the following major specific current applications for mercury in the three traditional use categories of the Bureau of Mines:

General Category	Specific Uses		
Electrical Apparatus	Batteries, lamps and power tubes		
Industrial & Control	(1) Switches		
Instruments	(2) Relays		
	(3) Others, including bar-		
	ometers, gauges, manometers, pump seals, thermometers and valves		
General Laboratory Use	Experimental equipment, an-		
	alysis, etc.		

In assessing these specific uses of mercury, a letter survey of 28 companies, representing the major producers of electrical apparatus and instruments was completed, with responses being obtained from 17 companies. In addition, numerous other individual contacts were made by phone and by letter. The results of these studies are summarized in Table 7, which includes for purposes of comparison, the Bureau of Mines 1968 statistics for these 3 general use categories. Pertinent comments on the specific applications are given as follow.

	Mercury Consumption, flasks					
	1968 Bureau of Mines Data			P	anel Estimat	tes
Use Category	Standard Allocation Report(a) of Redistilled(b)		Total	1968	1974	1979
l) Electrical Apparatus:						
Batteries				13,000	18,000	22,000
Lamps				1,200	1,700	2,400
Power Tubes				500	500	500
Unidentified	••			2,500	$\frac{2,500}{22,700}$	2,500
Subtotal	17,211	1,852	19,063	17,200	22,700	27,400
) Industrial & Control Instruments:						
Switches & Relays				2,500	2,650	2,800
Other Instruments				6,400	6,600	_6,800
Subtotal	2,841	4,124	6,965	8,900	9,250	9,600
3) General Laboratory Use:	1,202	926	2,128	2,075	2,075	2,075
Totals	21,254	6,902	28,156	28,175	34,025	39,075

# TABLE 7. CURRENT AND ESTIMATED MERCURY CONSUMPTION IN ELECTRICAL APPARATUS, INSTRUMENTS, AND LABORATORY USES

(a) Reported totals of four quarterly periods.

(b) Allocations of four quarterly totals according to 1967 percentile values from Footnote (a) of Table 4.

<u>Electrical Apparatus</u>. During 1968, it is estimated that over 13,000 flasks of mercury were used in the battery industry. Mercury is used in both the mercury cell and the alkaline energy cell where it is amalgamated with zinc to reduce hydrogen overvoltage. at the anode. It is also used as mercurous oxide in the cathode of the mercury battery where it acts as a depolarizer.

It is anticipated that, by 1974, over 18,000 flasks of mercury will be used by the battery industry and, by 1979, this segment of industry will be using over 22,000 flasks of mercury. To the best knowledge of this Panel, all such uses are satisfied by prime virgin grades.

Lamp industry projections indicate that mercury consumption in fluorescent and high intensity arc discharge lamps will double over the next ten years. Lamp uses will increase from a level of about 1,200 flasks in 1968 to 1,700 in 1974 and to 2,400 flasks in 1979. No substitutes are known for these uses of mercury in these applications.

Power rectifiers account for most of the mercury used in electron tubes. Consumption in 1968 will be about 500 flasks and will not likely rise above this level over the next ten years, since the market for mercury rectifiers is declining as a result of improving technology in solid state rectifiers.

To the best knowledge of this Panel, all of the mercury purchased for use in lamp or electron tube applications is of prime virgin grade. Before use, it is further purified by the individual lamp producers to insure that internal manufacturing specifications are satisfied.

The "unidentified" category was added into Table 7 by this Panel as a rough approximation of the amount of mercury consumed in numerous proprietary applications by the manufacturers of electrical

apparatus. This level of 2,500 flasks was left constant over the next ten years to reflect the probability that uses in this category are equally likely to increase or diminish.

Industrial & Control Instruments. The use of mercury in instruments such as pressure-sensing devices, thermometers, gauges, barometers, valves, pump seals, and meters is expected to see a general rise with a 7 percent increase in utilization between 1974 and 1979. Currently, over 6,400 flasks are used; and by 1979, this segment of the industry should be using in excess of 6,800 flasks per year of the mercury. Some substitutions will take place and they will be made with materials that can be considered nonstrategic in nature.

It is expected that the use of mercury in the switch industry will tend to decrease in the next ten years. The reduction will be due to changes in market, use of solid state switching devices, and reduction in the amount of mercury used in switching devices as a result of new design. This decrease can be as high as 10 percent in the 1974 to 1979 time period and will be a continuation of a trend that started in 1964. This change was partially brought on by the gross price fluctuations that have taken place in the mercury industry in the last ten years.

The relay industry will see a 7 percent increase in mercury utilization between 1974 and 1979. Some substitution will take place with solid state devices replacing electro mechanical relays in some applications.

The net results of the changes is that the industrial and control instruments segment of the industry will be using about 9,600 flasks of mercury per year by 1979, compared to 8,900 flasks in 1968.

As in the lamp industry, the major manufacturers of electrical switches and relays purchase selected prime virgin grades of mercury and purify this, as needed, to satisfy their internal manufacturing

specifications. Accordingly, the Panel assumes that some, although certainly not all, of the mercury going into the "Others" category of industrial and control instruments in Table 7 represents redistilled mercury.

<u>General Laboratory Uses</u> These uses are expected to continue at about the same level as for the past five years, i.e., from 1100 to 1200 flasks per year. Presumably, an additional 925<sup>(a)</sup> flasks of redistilled mercury should be added to this figure, giving an estimated total of about 2,075 flasks per year for the next 10 years.

Of the three general use categories considered, the Panel concludes that significant increases in consumption over the next five to ten years are likely to occur only in the area of electrical apparatus, principally in the use of mercury for batteries.

#### Electrolytic Preparation of Chlorine & Soda

Preliminary figures for 1968 and a 1975 forecast for mercury use in the production of chlorine are shown below:

	Estimated	No. of Flasks
	1968	1975
Chlorine Production New Chlorine Cell Require-	17,424	22,864
ments for Start-Up	7,815	$\frac{4,470 - 5,960}{27,334 - 28,824}$

The tabulation shows that chlorine production will require at least another 5,400 flasks in 1975 to offset mechanical losses of mercury during the manufacturing sequence. Requirements of mercury to activate new cell rooms are expected to be less in 1975 than in 1968, as a result of continuing process improvements. On a total

(a) On the basis of the 1967 percentile breakdowns given in Footnote(a) in Table 4.

demand basis for the chlorine industry, an additional 3,600 flasks above 1968 needs should be ample. Prime virgin mercury is satisfactory for all of these needs.

Based upon preliminary 1968 U.S. data for the manufacture of chlorine, 17,424 flasks of mercury were used, which represent an industry average of about 0.5 pound of mercury per ton of chlorine. Some plants operate at lower figures, while certain older facilities consume more mercury per ton of chlorine made.

During 1968, an identified 605 T/D (tons per day) of new mercury cell capacity began operating. The cells installed showed a wide variation relative to mercury needs per ton day, ranging from about 870 pounds to 1,400 pounds for each T/D of chlorine. An estimated 7,815 flasks were used to activate this new capacity, averaging about 980 pounds of mercury per ton of rated chlorine capacity. Government figures for these data are included in the "others" classification for mercury, issued by the Bureau of Mines.

Chlorine made directly from all sources experienced an average growth rate of  $7-^{3}/4$  percent annually in production for the period 1959-1968, according to the Chlorine Institute. It is expected that this growth will subside to 6 percent through the year 1975, owing to a slackening in overall nonendurable manufacturing. This is equivalent to 11.75 million tons of chlorine, which has been conservatively projected from a base of the average of the years 1964-1966. For simplicity, the 11.75 million tons demand is assumed to be identical to inplace capacity.

Across the past two decades, chlorine producers have shown a preference toward building more mercury cells, as shown by percentages of total capacity via this method. In 1946, a trifle over 4 percent of U.S. capacity was mercury cell. Ten years later, this figure had jumped to almost 12½ percent. In 1963, about 21 percent of chlorine capacity utilized mercury cells. Data for mid-1968 showed that about 28½ percent of all capacity was mercury! By 1975, it is expected that

a little over 38 percent of all production capacity will be mercury; of the total increase of 7,550 T/D expected to be added by that time about 4,530 T/D may be via mercury. This corresponds to 60 percent of the new construction.

There are a number of reasons why the use of mercury cells has become increasingly popular. Purity of products from these cells is superior to that available from diaphragm cells, an important consideration for certain markets. The shift in cell design to vertical decomposers from horizontal types plus the decreasing thickness of the mercury flowing through the cell have sharply decreased the amount of mercury needed for start up. Mercury cells have higher power consumption than diaphragm types. On the other hand, mercury cell derived caustic requires no steam for evaporation, a necessity for diaphragm liquor. Mercury cells are becoming increasingly larger with attendant efficiencies achieved by advanced engineering. Although economics have historically favored diaphragm cells, this increment has gradually narrowed and may be incidental within the near future.

It is expected that the mechanical losses of mercury in manufacturing will be reduced by 50 percent by 1975. By that time, it is likely that the average loss per ton of chlorine produced will be about & pound mercury. On this basis, the additional 4,530 T/D of chlorine will consume about 5,440 flasks of mercury. Combining this figure with 1968 capacity needs totals about 22,864 flasks in 1975.

A lessening in the quantities of mercury to charge new cells is expected to continue. Cells are now available which require a reported 700-pound mercury per ton day of chlorine. Using this figure as a guide, the projected 4,530 T/D of new mercury cell capacity will need about 41,720 flasks. Although chlorine cell expansions occur in surges, an even spread over 7 years implies that 5,960 flasks annually would be required.

A new permanent anode has been installed in 1969 in a major mercury cell plant, promising further improvements in capital costs for new facilities. Because of its ability to operate at higher current densities, mercury inventories on a basis of pounds per ton chlorine capacity should decrease about 25 percent. Should this anode achieve widespread acceptance in new plants, the average annual inventory demand may, theoretically, drop from 5,960 to 4,470 flasks.

A product for which an adjustment can be made is caustic potash. Part will be made in diaphragm cells, the remainder in mercury cells. There is adequate plant inplace today to make an estimated need of 202,000 tons of 90 percent KOH in 1975. This corresponds to an average growth rate of 2 percent.

A series of co-products are made with chlorine. Products such as metallic sodium and potassium nitrate may total 850 T/D equivalent in 1975. The 1975 chlorine routes are shown below:

> <u>1975 Chlorine T/D Capacity</u> Chlorine Available for Caustic Soda Total Diaphragm Mercury Others 32,700 19,360 12,490 850

When the individual market segments of KOH are projected ahead, a number of uses show a growth rate of at least 2½ percent. Such outlets include industrial chemicals, soaps and detergents, potassium carbonate and petroleum refining. Demand for tetrapotassium pyrophosphate in 1975 is expected to be less than that of recent years.

Deducting the caustic potash equivalent as chlorine leaves the available, residual capacity to make caustic soda.

<u>1975 Chlorine T/D Capacity</u>							
Chlorine Available for Caustic Soda							
Total	Disphragm	Mercury	<b>Others</b>				

There is a small, residual tonnage of additional caustic potash capacity arbitrarily assigned to caustic soda. This will show no practical error inasmuch as some producers shift from one alkali form to the other by changing brine feed to the cells.

#### Paints

Organomercurial compounds are the most widely used bactericide/ fungicide products in the paint industry accounting for about 80 percent of dollar sales. Efficiency/cost comparisons with other preservatives invariably demonstrate the superiority of mercurials in providing both shelf preservation and exterior protection. No development has been detected that is likely to change this situation greatly in the next five or six years. In fact, the paint industry requirements of three to four years of field testing before widespread adoption of a new compound provides a buffer against rapid obsolescence. Industry needs will grow with the growth of water-based paints for interior and exterior applications.

Inorganic mercurials as toxicants in anti-fouling marine paints will not increase unless a national emergency or an international crisis develops that would create a demand for government specification formulations which include the anti-fouling mercurials.

The following represents the mercury consumed in the United States for the last few years and estimated requirements for the next several years:

<u>Use</u>	<u>1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>	<u>1974</u>
Anti-fouling	400	375	375	350	350	325
Mildewproofing	9,000	<u>9,575</u>	9,625	9,650	<u>9,650</u>	9,675
Total	9,400	9,950	10 000	10, 000	10,000	10,000

<u>Mildewproofing Substitutes.</u> In case of a national emergency, non-metallic organic preservatives could be substituted for organomercurials. This substitution would increase paint manufacturers' costs for preservation (not prohibitively) and also would necessitate dating the container for maximum period of shelf storage or field checking at stated periods for putrefaction.

For exterior paint formulations, the omission of an organomercurial mildew inhibitor would lessen the life (at least 25 percent) of the paint film increasing the need of repaint (more paint requirements). Other organometallics (tin, arsenic, lead, zinc) may be substituted; however, these will not attain the same performance and will have the further disadvantage of higher costs for the manufacturers. Formulation changes, e.g., inclusion of zinc oxide, may improve mildew resistance but will sacrifice other desirable paint properties.

Research studies are underway in several laboratories directed toward replacement of organomercurials as mildew inhibitors. Thus, it is expected that new products should appear within three or four years.

<u>Anti-fouling Substitutes.</u> Hot plastic, vinyl, and polyisobutylene anti-fouling formulations seem to fulfill at present the Navy requirements to keep a ship "out of dock" for at least 18 months. These formulations are based on cuprous oxide. However, no anti-foulant toxicants, except for mercurial compounds, have been found to control the slime film which provides a favorable foothold, in most cases, for marine growth. Thus, in the case of a national emergency, one policy decision would be whether or not to use mercurial toxicants primarily to control the formation of slime film, especially on capital ships. Should the decision be to use mercurial toxicants, mercury requirements to manufacture the anti-fouling compounds would be 1,500-2,000 flasks for initial needs, reducing to 1,000 flasks the following years.

In summary, in the case of national emergency, the need for mercurial fungicides could be cut drastically by substituting higher cost non-mercurial biocides. However, the Navy might increase needs to 1,500-2,000 flasks per year.

### Paper & Pulp

The substantial use of mercury compounds during the early 1960's as slimicides in the pulp and paper industry has continued to decline within the past three years. The primary factors for the decline have been:

- The Food and Drug Administration's rulings on compounds which are used in the manufacture of paper or board, which may come in contact with food.
- (2) The introduction of effective non-mercurial biocides.
- (3) The higher cost of mercury and mercury compounds and the widely fluctuating pricing resulting from erratic market activities.

Although lower usage is anticipated, the decline will probably be at a much lower rate than it has been in the last five years. The high degree of effectiveness of these compounds and their ability to perform where other types of products have failed seems to indicate there will be a market for these types of products for at least the next five years.

The following estimate of the market for mercury based products to be used as slimicides in the pulp and paper industry is forecast for the next five years, purely on the basis of estimated sales of such products by industry suppliers.

	<u>1968</u>	<u> 1969</u>	<u>1970</u>	<u>1971</u>	<u>1972</u>	<u>1973</u>
Approx. Flasks	375	349	317	279	252	252

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In case of national emergency and severe allocation, all mercurial slimicides could be effectively replaced by presently available non-mercurial products. The substitution could be accomplished without disruption and undue cost to the paper industry.

#### Pharmaceuticals

Mercury is used in a variety of well-defined pharmaceutical and cosmetic applications. These include diuretics, antiseptics, skin preparations, and preservatives. Based on the current marketing research conducted in support of this Panel, the 1968 consumption may be summarized as follows:

Use	1968, Flasks		
Diuretics	100		
Antiseptics	260		
Skin Preparations	200		
Preservatives	<u>    40    </u>		
Total	600		

Detailed descriptions of these applications for mercurials are:

<u>Diuretics</u>. Organic mercury compounds have been used as diuretics for many years, but over the past 5 to 10 years, they have fallen out of favor and have declined in use. Non-mercurials as effective as the mercury compounds for most applications have grown. Nonetheless, these mercurial diuretics are extremely fast acting and powerful, and it is unlikely that their usefulness will decline to zero. The current market is estimated as consuming 100 flasks, but this will decline to perhaps 75 flasks in 1973.

<u>Antiseptics</u>. The major market for mercurials as antiseptica is in organic compounds, usually sold under proprietary names, such as: Merthiolate (Lilly); Mercurochrome (Hynson, Westcott and Dunning); Metaphen (Abbott); and Mercresin (Upjohn). This market has been growing slowly but measurably, and is currently estimated at 210 flasks of mercury. These particular compounds matured many years ago and have

essentially followed population growth trends, while other antiinfectives have been growing more rapidly.

An additional market for mercury in this application is the use of inorganic mercury salts such as mercuric chloride or mercuric cyanide as components of solutions for sterilization of instruments, etc., in hospitals or doctors' offices. This application uses an estimated 50 flasks per year.

The use of mercury in these two segments of the antiseptic market will probably remain constant over the next 5 to 10 years.

Skin Preparations. Mercury compounds are used in a variety of therapeutic and cosmetic skin creams. The smaller market uses probably 50 flasks per year in the form of ammoniated mercury, yellow mercuric oxide, or prime virgin mercury ("blue ointment") for various skin ailments.

A much larger use is skin creams containing ammoniated mercury which are used to "fade blemishes, brown spots, and dull dark areas."

The therapeutic uses of mercury will probably decline over the next five years while the cosmetic uses should increase, perhaps 50 percent to 1973; a probable number for 1973 would be 275 flasks.

<u>Preservatives</u>. There is a relatively small, perhaps 40 flasks per year, market for phenyl mercurials in cosmetics, soaps, as preservatives; similarly many portions of animal carcasses used for extraction of drug components are preserved with these phenyl mercurials. Mercurials used include phenyl mercuric acetate, phenyl mercuric borate, phenyl mercuric benzoate, phenyl mercuric nitrate.

Overall uses of mercury in the previously described pharmaceutical applications should grow slightly, perhaps to 650 flasks per year in 1973.

Although substitutions are possible in each and every one of the areas of mercury use, in time of critical supply it would probably suffice to discontinue the use of mercury in cosmetic skin preparations which would reduce the consumption by 150 to 200 flasks per year. None of the other applications is extremely large, and although substitutions <u>are possible, mercury's uses in these few small areas probably would be</u> better left alone.

#### Other Possible Uses

As a part of this Panel's assignment, an assessment was made of various government-sponsored research and development programs in which mercury and/or its compounds are being evaluated. The intent of this review was to identify, if possible, any potential new uses for mercury which might lead to significant increases in the demand for mercury over the next 5 to 10 years.

The result of this search was largely negative despite the fact that two current R&D evaluations involving mercury are showing some promise.

One of these potential applications involves the use of mercury as a heat transfer medium in nuclear space power generators, e.g., the SNAP-2 and SNAP-8 experimental reactors<sup>(a)</sup>. The corrosion problems associated with mercury are severe, and the current annual consumption of mercury in these programs was estimated at 7 flasks. In five years, these requirements could reach 20 flasks, and in ten years, this level might reach 40 flasks or zero.

In other development work, dilute mercury-gold alloys are showing promise as an electrical contact material in reedswitches. These are low energy contact switches which are used in great profusion in telephone and computer circuits. However, the total quantity of mercury

<sup>(</sup>a) The use of mercury for similar purposes in steam power generation, while once important, is no longer of commercial significance.

required in each switch is extremely small, i.e., of the order of less than 3 milligrams. Thus, even if the requirements for these should reach the rather optimistic level of 100 million switches per year by 1975, the total quantity of mercury involved would be less than 10 flasks per year.

#### Specifications for Stockpile Purchasing

National Stockpile Specification P-31-R1 of May 27, 1958, was reviewed by this Panel and found to be adequate in all respects.

# Summarized Trends

Table 8 presents a summary of the estimated current and future use pattern of mercury over the next 5-year period.

Of the ll major categories represented, increasing demands are forecast in seven including catalysts, dental preparations, electrical apparatus electrolytic preparation of chlorine and soda, industrial and control instruments, paints, and pharmaceuticals. Of this group, by far the greatest growth is expected in the areas of electrical apparatus (specifically battery applications) and in the electrolytic preparation of chlorine which uses are expected to increase by 36 to 39 percent in the next 5 years.

General laboratory uses are expected to continue at about the same level while decreasing levels of mercury consumption are indicated in agriculture, amalgams, and paper and pulp.

The net result of these trends is that by 1974-1975, the total consumption of mercury is expected to increase above the present indicated level of 73,855 flasks by about 9,690 flasks. This represents an overall increase of about 13 percent.

# TABLE 8. ESTIMATED TRENDS IN CONSUMPTION OF MERCURY

	الداكة فعردت الكافلاجي والزدارات		
	Estimated Mercury		
	Consumption, flasks		
Use	1968	1974-1975	
Agriculture	3,430	2,650	
Amalgams	259	250	
Catalysts:			
Urethanes	800	1,560	
Vinyl Chloride Monomer	500	250	
Anthraquinone Derivatives	175	220	
Miscellaneous	236	340	
Dental Applications	$3,500^{(a)}$	$3,800^{(a)}$	
Electrical Apparatus	17,200	22,700	
Electrolytic Preparation of			
Chlorine & Soda	17 626	22,864	
General Laboratory Use	17,424 2,075(a)	2,075(a)	
Industrial & Control Instruments:	2,075	2,075	
Switches & Relays	2,500	2,650	
Other Instruments	$6,400^{(a)}$	2,050(a) 6,600 <sup>(a)</sup>	
Paints	10,566	10,725	
Paper & Pulp	375	250	
Pharmaçeuticals	600	650	
Others <sup>(b)</sup>	7,815	5,960	
Totals	73,855	83,544	

(a) Includes some redistilled mercury.

(b) Includes mercury requirements for start-up of new chlorine cells.

## CONCLUSIONS

(1) The consumption of mercury in electrical apparatus (most notably in batteries) and in the electrolytic preparation of chlorine and soda has clearly dominated all other uses and will continue to do so over the next 5 to 10 years.

(2) Increasing demands for mercury are also forecast over the next 5 years in the areas of catalysts, dental preparations, industrial and control instruments, paints, and pharmaceuticals.

(3) No significant changes and/or declining levels of mercury consumption are indicated in general laboratory uses, agriculture, amalgamation, and in the paper and pulp industries.

(4) The result of these trends is that mercury consumption in the United States is expected to increase from its current level of about 73,855 flasks to about 83,544 flasks in 1974-1975.

(5) No new applications or uses for mercury are evident which will significantly affect its usage pattern over the next 5 to 10 years.

(6) The quality of mercury being stockpiled by the General Services Administration is adequate for the projected markets.

Trends in Usage of Mercury http://www.nap.edu/catalog.php?record\_id=20533

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