

**EMISSION STUDY  
OF INDUSTRIAL SOURCES  
OF LEAD AIR POLLUTANTS  
1970**



**U.S. ENVIRONMENTAL PROTECTION AGENCY  
Office of Air and Water Programs  
Office of Air Quality Planning and Standards  
Research Triangle Park, North Carolina 27711**

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OF LEAD AIR POLLUTANTS  
1970**

by

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## PREFACE

This report was prepared by W. E. Davis & Associates pursuant to Contract No. 68-02-0271 with the Environmental Protection Agency, Office of Air Programs.

The inventory of atmospheric emissions has been prepared to provide reliable information regarding the nature, magnitude, and extent of lead emissions from industrial sources in the United States for the year 1970.

Background information concerning the basic characteristics of the lead industry has been assembled and included. Process descriptions are given, but they are brief, and are limited to the areas that are closely related to existing or potential atmospheric losses of the pollutant.

Due to the limitation of time and funds allotted for the study, the plan was to personally contact all of the primary producing companies and about seventy-five percent of the large industrial users of lead in each emission source group to obtain the required information. It was known that published data concerning the atmospheric emissions of lead were virtually nonexistent, and contacts with industry ascertained

that atmospheric emissions were seldom a matter of record. The lead emissions and emission factors that are presented are based on the summation of data obtained from industrial sources. Additional information was acquired during field trips to inspect air pollution control equipment and observe processing operations.

## ACKNOWLEDGEMENTS

This was an industry-oriented study and the authors express their appreciation to the many companies and individuals in the lead industry for their contributions.

We wish to express our gratitude for the assistance of the various societies and associations, and to the many branches of the Federal, State, and Local Governments.

Our express thanks to Mr. C. V. Spangler, Project Officer, EPA, Office of Air Programs, Research Triangle Park, N. C., for his helpful guidance.

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## INTRODUCTION

The primary objective of this study was to investigate and determine the nature, magnitude, and extent of industrial lead emissions to the atmosphere in the United States during the year 1970. The emission estimates, the particle size distribution, the chemical analyses, and the air pollution control equipment data presented herein represent a broad spectrum of information from numerous sources.

The many industrial processes and activities that generate significant lead emissions to the atmosphere are described in this report so that the reader may have the opportunity to understand why there are such great variations in the magnitude of emissions from different sources. Information on the efficiency and effectiveness of various air pollution controls is included and compared,

It should be pointed out that this document does not include estimates of lead emissions from natural sources, emissions due to the burning of leaded gasoline, or others not directly related to industrial activities such as resuspension of lead by moving vehicles, burning of lead-painted surfaces, welding of lead-painted steel, dusting of lead-containing items subject to weathering, and incineration of leaded plastics.

## SUMMARY

The flow of lead in the United States has been traced and charted for the year 1970 (Figure I). The consumption was 1,361,000 tons, while primary and secondary production totaled 667,000 and 597,000 tons, respectively. Approximately 20 percent of the primary lead was recovered from foreign ore.

Emissions to the atmosphere during the year were 18,050 tons (Table I). About 18 percent of the emissions resulted from the burning of waste oil, 13 percent from municipal incineration, 13 percent from grey iron foundries, 11 percent from the processing of gasoline additives, 9 percent from the production of primary lead, 9 percent from copper smelting, and 8 percent from the production of iron and steel. The combustion of coal, the manufacture of storage batteries, and the production of portland cement were also significant emission sources.

Emission estimates for mining, production of primary and secondary lead, lead oxide processing, and the manufacture of end use products are based on unpublished data obtained from industrial sources.

TABLE I

EMISSIONS BY SOURCE  
1970

<u>Source Category</u>	<u>Source Group</u>	<u>Emissions - Tons</u>	<u>Emissions %</u>
Mining and Milling		60	0.3
Metallurgical Industries		3,860	21.4
	Primary Lead	1,700	
	Primary Copper	1,700	
	Primary Zinc	240	
	Secondary Lead	220	
Lead Oxide		140	0.8
Consumer Product Manufacturing		3,080	17.0
	Storage Batteries	480	
	Gasoline Additives	1,400	
	Pigments	210	
	Solder	110	
	Cable Covering	50	
	Type Metal	200	
	Brass and Bronze	40	
	Metallic Lead Products	90	
Other Emission Sources		10,910	60.5
	Waste Incineration		
	Waste Oil	3,200	
	Municipal Incineration	2,400	
	Sewage & Sludge Incineration	200	
	Coal	650	
	Oil	90	
	Iron & Steel	1,500	
	Grey Iron Foundries	2,300	
	Ferroal	70	
	Cement	500	
		18,050	100.0

TABLE II  
EMISSIONS BY STATES

<u>State</u>	<u>Tons</u>	<u>State</u>	<u>Tons</u>
Alabama	273	Nebraska	73
Arizona	1,012	Nevada	126
Arkansas	160	New Hampshire	35
California	1,123	New Jersey	797
Colorado	103	New Mexico	167
Connecticut	154	New York	1,044
Delaware	26	North Carolina	261
Florida	330	North Dakota	30
Georgia	367	Ohio	829
Idaho	1,066	Oklahoma	165
Illinois	882	Oregon	120
Indiana	597	Pennsylvania	1,199
Iowa	137	Rhode Island	45
Kansas	158	South Carolina	134
Kentucky	164	South Dakota	35
Louisiana	1,112	Tennessee	232
Maine	50	Texas	1,374
Maryland	193	Utah	475
Massachusetts	279	Vermont	22
Michigan	702	Virginia	242
Minnesota	171	Washington	164
Mississippi	122	West Virginia	99
Missouri	643	Wisconsin	223
Montana	320	Wyoming	15
TOTAL			18,050

### EMISSION FACTORS

The emission factors presented herein are the best currently available. They were determined through a combination of methods consisting of: (1) direct observation of emission data and other related plant processing and engineering data; (2) estimates based on information obtained from literature, plant operators, and others knowledgeable in the field; (3) calculations based on experience and personal knowledge of metallurgical processing operations; and, (4) specific analytical results where available.

The basic data used to calculate the emission factors are contained in the files of the Contractor.

TABLE III  
EMISSION FACTORS

<u>Source</u>	<u>Factor</u>	<u>Qualifier</u>
Mining and Milling	0.2 lb/ton lead mined (controlled)	Plant visit
Metallurgical Industries		
Primary Lead Production	5.0 lb/ton of product (controlled)	Questionnaires
Primary Copper Production	0.6 lb/ton of Cu concentrates (controlled)	Estimate
Primary Zinc Production	0.3 lb/ton of Zn concentrates (controlled)	Estimate
Secondary Lead Production	0.7 lb/ton of product (controlled)	Questionnaires
Lead Oxide Processing	0.7 lb/ton of lead oxide (controlled)	Questionnaires
Consumer Product Manufacturing		
Storage Batteries	8.0 lb/ton of lead processed (uncontrolled)	Questionnaires
Storage Batteries	1.3 lb/ton of lead processed (controlled)	Questionnaires
Gasoline Additives	14.0 lb/ton of lead processed (controlled)	Questionnaires
Solder	3.0 lb/ton of lead processed (controlled)	Estimate
Cable Covering	2.0 lb/ton of lead processed (controlled)	Questionnaires
Type Metal	17.0 lb/ton of lead processed (controlled)	Questionnaires
Brass and Bronze	4.0 lb/ton of lead processed (controlled)	Questionnaires

## Other Emission Sources

Waste Oil Combustion	0.04 lb/bbl of oil burned (controlled)	Estimate
Municipal Incineration	0.2 lb/ton of charge (controlled)	Stack sampling
Sewage and Sludge Incineration	0.6 lb/ton of charge (uncontrolled)	Stack sampling
Coal Combustion	2.2 lb/1,000 tons of coal burned (controlled)	Estimate
Distillate Oil Combustion	0.1 lb/1,000 bbls of oil burned (uncontrolled)	Stack sampling
Residual Oil Combustion	0.04 lb/bbl of oil burned (uncontrolled)	Stack sampling
<b>Steel Production</b>		
Open-Hearth	0.14 lb/ton of steel (uncontrolled)	Atomic absorption
Basic Oxygen	0.18 lb/ton of steel (uncontrolled)	Atomic absorption
Electric Arc	0.18 lb/ton of steel (uncontrolled)	Atomic absorption
Grey Iron Foundries	0.3 lb/ton of iron (uncontrolled)	Estimate
Cement Production	25 lb/1,000 bbl of cement production (uncontrolled)	Stack sampling
Pigments	10 lb/ton of lead processed (uncontrolled)	Questionnaires
<b>Ferroalloys</b>		
Silicomanganese Electric Furnace	0.9 lb/ton of product (uncontrolled)	Estimate
Ferromanganese Electric Furnace	0.4 lb/ton of product (uncontrolled)	Estimate
Blast Furnace	4 lb/ton of product (uncontrolled)	Estimate



### SOURCES OF LEAD

Lead (Pb) is a heavy, soft, bluish-gray, corrosion-resistant metal that is widely distributed in the earth's crust in the form of its various minerals. It occurs commonly as galena (lead sulfide,  $\text{PbS}$ ), cerrusite (lead carbonate,  $\text{PbCO}_3$ ), and anglesite (lead sulfate,  $\text{PbSO}_4$ ). In the United States the most abundant lead mineral currently mined is galena and it is often associated with the zinc mineral, sphalerite, commonly called zinc blende.

The ratio in which lead and zinc minerals are found in combination varies over a wide range. In Missouri, the leading lead-producing state, the ratio is in the order of 90 percent lead to 10 percent zinc. In the eastern states the situation is quite different; the ores there contain only a small amount of lead. Ores found in the western states contain approximately equal parts of the two minerals.

In the United States the supply of lead during 1970 was derived from four sources: secondary lead reclaimed from new and old scrap, primary lead produced from domestic ores, imported metal, and primary lead recovered from

foreign ores. Secondary lead is very important in the domestic supply pattern. In fact, since 1945 the quantity of lead from this source has exceeded domestic mine production. Battery plates, cable covering, pipe, and sheet lead are the principal scrap materials that are reclaimed for remelting and refining.

During 1970 a large part of the domestic lead ore was produced in the southeastern part of Missouri. The quantity of ore mined in the state totaled nearly 9 million tons and the recoverable lead content was reported at 421,764 tons  $\frac{1}{2}$ , or approximately 74 percent of the domestic production.

The recoverable lead content of ore produced in Idaho, Utah, and Colorado was 61,211 tons, 45,377 tons, and 21,855 tons, respectively. Other states producing less than 6,800 tons included Arizona, California, Kansas, Montana, Nevada, New Mexico, New York, Virginia, Washington, and Wisconsin.

Mine production of lead in the world during 1970 was nearly 3.8 million tons of which nearly 32 percent was produced in North America, over 7 percent in South America, 31 percent in Europe, about 6 percent in Africa, nearly 9 percent in

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

Asia, and more than 13 percent in Australia 1/. There were 3 producing countries in North America, 2 in Central America, 6 in South America, 20 in Europe, 6 in Africa, and 11 in Asia. Imports of metal and ore into the United States were principally from Australia, Canada, Honduras, Mexico, Peru, Republic of South Africa, and Yugoslavia.

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

### MATERIAL FLOW THROUGH THE ECONOMY

The consumption of lead in the United States during 1970 was 1,360,552 tons <sup>1</sup>/<sub>-</sub>, a decline of about 2 percent from the previous year. Smaller quantities were required in nearly every phase of industry except for motor vehicles, where approximately 2 percent more was used for production of storage batteries and gasoline antiknock additives.

The sources of supply were principally as follows: primary lead, 528,086 tons produced from domestic ores and 138,644 tons from foreign ores; secondary lead, 597,390 tons recovered from salvage materials; and imported metal, 244,623 tons <sup>1</sup>/<sub>-</sub> as shown in Figure I. Most of the antimonial lead, solder, and type metals were produced as secondary metal.

The largest consumption of lead was in storage batteries. About 44 percent of the total supply was utilized for this purpose. The second largest use, slightly more than 20 percent, was in the production of gasoline antiknock additives. Other

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

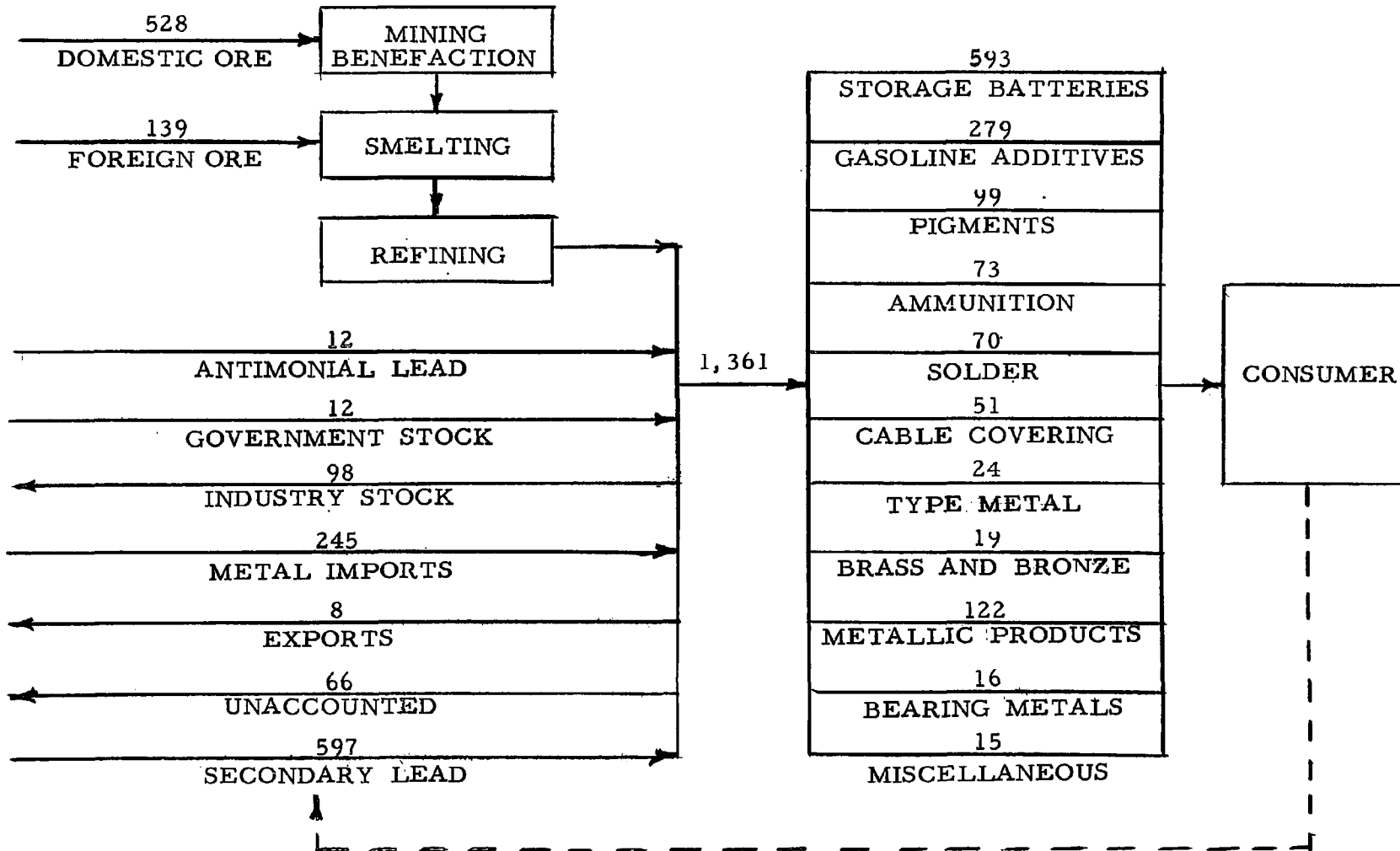
# LEAD

## MATERIAL FLOW THROUGH THE ECONOMY - 1970

(1,000 Short Tons)

### SOURCES

### USES



specific products requiring from 25,000 to 100,000 tons each were pigments, ammunition, solder, cable covering, and caulking lead. Categories of use requiring less than 25,000 tons included type metal, sheet lead, brass and bronze, piping materials, bearing metals, weights and ballasts, collapsible tubes, castings, foil, terne metal, galvanizing, annealing, and glass.

## USES AND EMISSIONS OF LEAD

### MINING AND MILLING

The lead ores produced from underground mines in Crawford, Iron, Reynolds, St. Francois, and Washington counties in the southeastern part of Missouri accounted for about 75 percent of the lead recovered from domestic ores during 1970. The average lead content of these ores was 4.8 percent, and the zinc concentration was 0.6 percent  $\frac{1}{2}$ .

Even though the practices followed at different mining locations vary somewhat, the basic operations that are performed are essentially the same. In the typical mine, percussive drilling machines and metallized explosives are used to loosen and break the ore. The operations that follow include ore loading, moving, crushing, and hoisting as shown in Figure II.

After the ore reaches the surface the size reduction process continues as the material passes through primary screening, secondary crushing, secondary screening, tertiary crushing, and milling. At this point the ore is in a very finely divided

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

TYPICAL FLOW DIAGRAM  
LEAD MINING AND MILLING

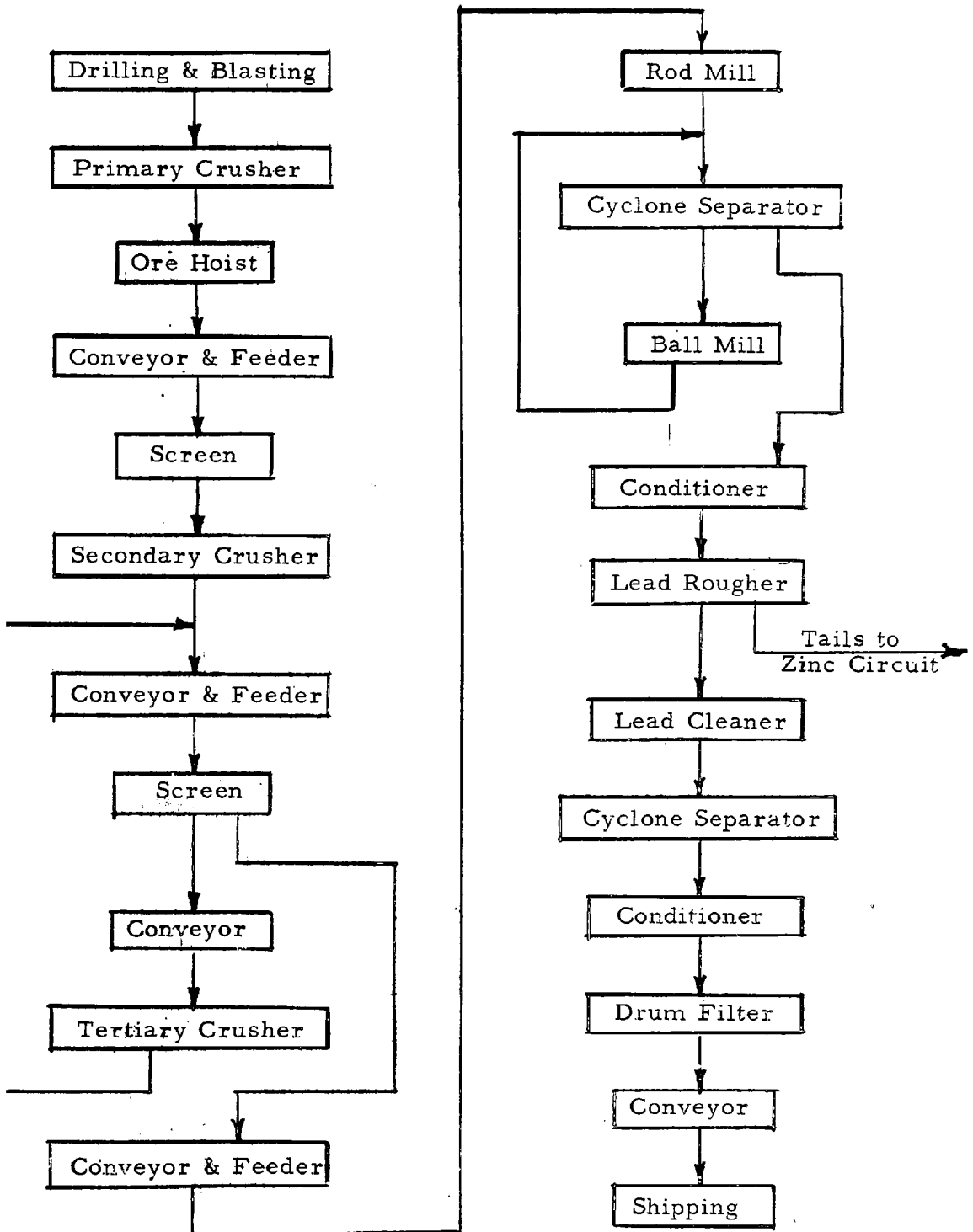


Figure II



state and is ready for separation by selective flotation.

First the lead concentrates are separated in the lead flotation rougher and processed in a cleaner, a thickener, and a filter as they are prepared for shipment to the smelter. The zinc concentrates are separated in the zinc flotation rougher, and the final step is to forward tailings to the tailings pond.

From the standpoint of emissions to the atmosphere, the principal losses during mining and milling operations are those that occur due to ore handling, screening, crushing, and wind loss from outdoor storage of concentrates. During grinding and flotation, the ore is wet and atmospheric emissions are negligible.

While this study was in progress, many lead mining companies were contacted regarding their operations and the lead emissions that occur prior to the time concentrates are shipped to the smelter. Records and test data on lead emissions were not available; however, numerous emission sources were observed at each location which was visited.

Lead emissions to the atmosphere from sources of mining and milling are based on visual inspections and estimated by the Contractor at 0.2 pound per ton of lead mined. The

recoverable lead content of the ore mined in the United States during 1970 was 571,767 tons  $\frac{1}{\text{ton}}$ , and lead emissions to the atmosphere were 60 tons.

It is estimated that each of the seven leading lead-producing mines in the United States in 1970 produced ore containing 26,000 tons or more of lead, and lead emissions from each mine are potentially more than 20 pounds of lead per day. Six of the mines are located in Missouri and one in Idaho.

## PRIMARY LEAD

In the United States primary lead is recovered principally from ores that contain varying amounts of galena (lead sulfide) and other minerals. The ore, as mined, also contains a large quantity of nonvaluable material that is separated from the minerals as the ore is upgraded during the flotation-concentration process. These separations, however, are not complete and the lead concentrates carry with them many impurities that must be removed from the lead by means of three basic pyrometallurgical processing steps. These basic steps are essentially the same at all smelting and refining facilities. They are sintering, blast furnacing, and refining.

Even though there are differences in the ores and concentrates, in a modern plant the major smelting and refining equipment is of similar design. Lead sulfides are converted to oxides of lead and sulfur at a relatively low temperature in an updraft sintering machine. Then, the oxidized material is reduced with coke at a high temperature in a blast furnace to form lead bullion. During both these processing steps, considerable quantities of waste gases containing lead are discharged from the equipment. After smelting, the

lead bullion is transferred to the refining section where several large open-refining kettles are utilized for the removal of copper, silver, zinc, and other impurities.

The principal raw material in primary lead smelting is a lead sulfide concentrate containing about 60 to 70 percent lead, 6 to 7 percent zinc, 13 to 18 percent sulfur, up to 5 percent iron, and small quantities of lime, silica, silver, gold, arsenic, cadmium, selenium, tellurium, and other substances. The flux materials are silica, limestone, granulated slag, and small amounts of scrap iron, which are used in the proportions required to produce a free-running slag. The concentrates, coke, flux materials, and direct smelting ores are received at the various smelters by railroad or by truck; therefore, the methods of handling are somewhat different. At one location the concentrates are received in hopper-bottom trucks, transferred to hopper-bottom railroad cars, weighed, sampled, and dumped into large, covered, storage bins. Wind losses of lead at this location are relatively minor compared to those at another plant where concentrates are received both by truck and by rail, then stored outdoors.

As the raw materials are needed the concentrates, flux materials, direct smelting ores, return sinter, and return dusts are sized, measured, and mixed as required for the feed to the sinter machine, as shown in Figure III. During these operations conveyors are used to transfer the materials and there are some lead emissions to the atmosphere.

The purpose of sintering is to remove sulfur and produce a calcine that is strong, porous, and suitable for reduction in the blast furnace. By roasting, the sulfide concentrates are converted to oxides and the sulfur is reduced to an acceptable limit of approximately one percent. About 85 percent of the sulfur in the feed is emitted with the off-gas and 14 percent appears in the slag and other solid by-products. As the lead and other metal sulfides are oxidized, heat is generated and must be controlled to prevent excessive loss of metals by volatilization. The temperature should be held below 1,400 F.

The updraft sintering machine is a continuous conveyor with a windbox located above the moving grate-bar pallets.

There are two feeders in series. The first deposits a thin layer of feed material which is ignited before it reaches the

TYPICAL LEAD SMELTER-REFINERY  
FLOW DIAGRAM

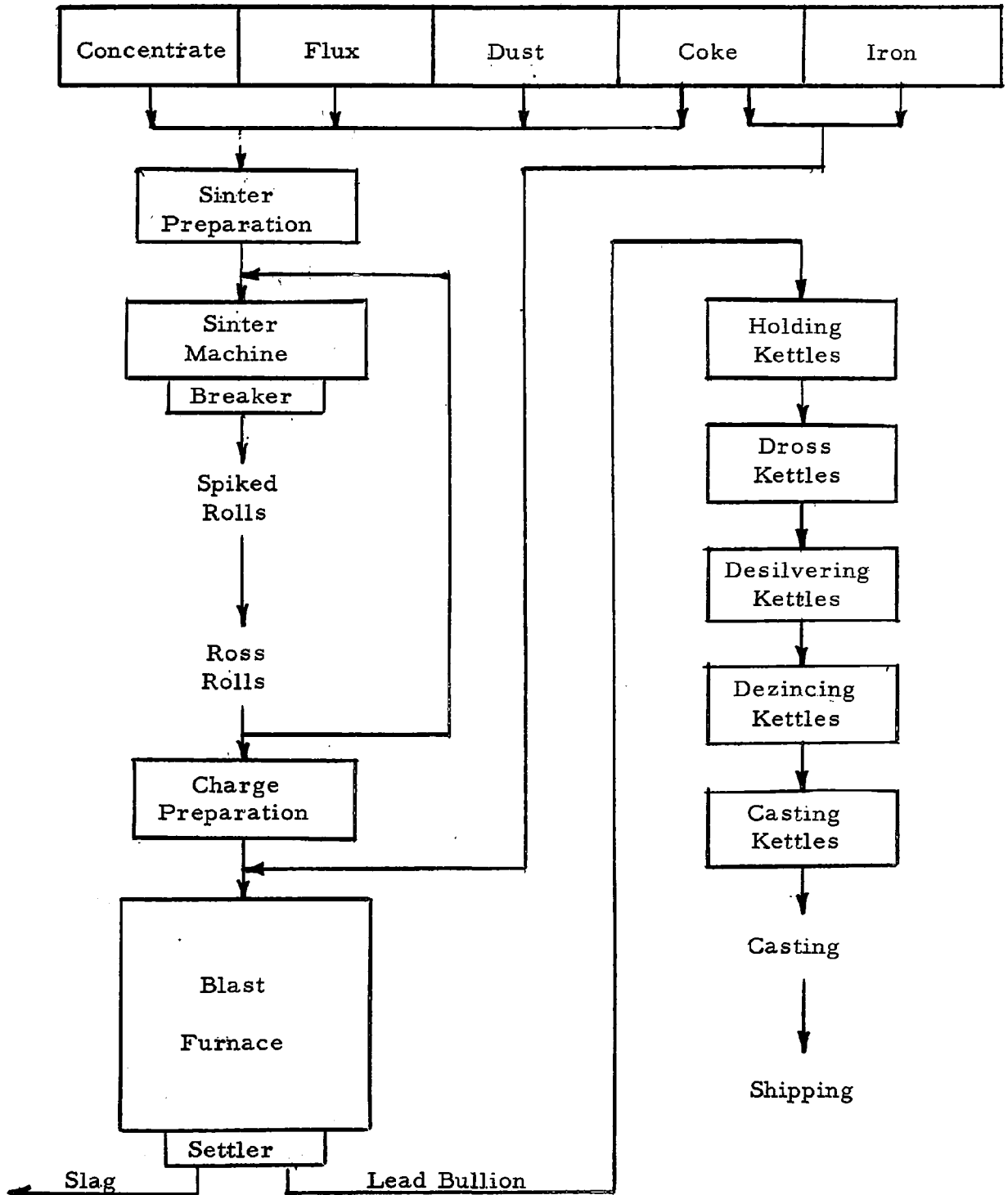


Figure III

point where the main layer is discharged from the second feeder. Regulated updraft causes the burning to progress from bottom to top, while gases, dust, and fume are drawn through the upper windbox into ducts leading to the dust collecting equipment.

The dust, including condensed fume, is recovered in bag filters and recycled to the feed for the sintering machine. It contains portions of all the elements present in the concentrates and is relatively rich in the more volatile metals. Such condensation and recycle of fume provides an opportunity for recovering cadmium, which becomes more and more concentrated during continued recycling. Usually when the cadmium concentration reaches about 10 percent, the dust is diverted to cadmium recovery facilities. After dust recovery in the bag filters, the off-gas from the feed end of the updraft sinter machine may be used as the feed to a sulfuric acid plant. This is the current method at some lead smelters.

In modern practice the smelting of lead is carried out in blast furnaces in which the charge of sinter, limestone, silica, and coke is heated and blown with air to effect the

reduction of lead oxide to metallic lead. Complete combustion of some of the coke supplies heat required for the principal reaction and various others that take place. Heat is released as the carbon in the coke combines with the oxygen in the air to form carbon dioxide. The remaining coke, the carbon dioxide, and the heat react to form carbon monoxide which is the reducing agent for the lead oxide.

The products generated in the blast furnace consist of four liquids and the flue gas. The liquids, lead bullion, matte, speiss, and slag are removed from the bottom of the furnace and fed into a forehearth where the products separate into layers before they are drained. The slag, containing 10 to 20 percent zinc and perhaps 2 percent lead, is usually granulated in water and forwarded to the dump. The lead bullion is transferred to the refinery. The matte and speiss, containing 40 to 65 percent copper and 8 to 20 percent lead, are of relatively minor value and usually are shipped to other metallurgical plants. The gases, dusts, and fumes emitted from the furnace are collected and cleaned in a bag filter before the off-gas is released to the atmosphere.

The differences in lead smelting practice are principally



due to variations of the impurities in the ores, the handling of materials, and the degree of completeness of processing. Certain metallic contaminants are reduced with the lead and a subsequent refining process is required. Other contaminants affect the composition of the slags that are rejected from the process.

At most lead smelters there is refining equipment that includes lead kettles for holding, drossing, desilvering, dezincing, and casting. Drossing is carried out by slowly melting the bullion at controlled temperatures to remove trace copper, tin, antimony, and arsenic. These contaminants are preferentially oxidized and removed by skimming from the molten lead. Lead from the reverberatory furnace is transferred to desilvering kettles to which zinc is added to form a crust containing the gold and silver. The crust is removed for further processing and the lead is transferred to dezincing kettles where the residual zinc is removed by distillation under vacuum. Usually at this stage the lead bullion is treated with caustic for removal of the last traces of impurities. The refined lead is then tapped and cast.

From the standpoint of lead emissions to the atmosphere,

there are many sources at lead smelters that should be considered in an emission inventory. Usually, however, the metallurgical operations have been regarded as the most important; this is the area in which there is a limited amount of published information. The other emission sources, often overlooked and rarely included in emission estimates, are materials transportation, handling, and storage. Relatively large quantities of particulates, including lead, are emitted from outside storage of concentrates and from railroad cars or trucks carrying the concentrates from mining areas to the smelter locations. Considerable dust with high lead content is transported by winds to areas far from the smelter site.

Emissions from metallurgical operations originate at the sintering machine, the blast furnace, the reverberatory furnace, and the refining kettles. During 1970, at smelters producing more than 85 percent of the lead, the off-gases from the sintering machines were cleaned either in a baghouse or in gas-cleaning equipment near their acid plants. At one plant these gases were cleaned in an electrostatic precipitator. At all smelters the blast furnace gas was discharged through a baghouse. At the refineries handling about 60

percent of the lead, gases from the dross reverberatory furnaces were directed through a baghouse.

During this study all primary lead smelters and refineries were contacted regarding their operations and their lead emissions to the atmosphere. Information was obtained from all smelters; however, it was incomplete in some instances. Based on the information that was received, the lead emissions to the atmosphere during 1970 due to the smelting and refining of primary lead totaled 1,700 tons, including windblown losses estimated at 350 tons. Lead emissions from the various metallurgical operations range from less than one to 14 pounds per ton of lead produced, averaging 4 pounds per ton, while windblown losses average approximately 1 pound per ton.

Emissions from the stacks were principally lead oxides. The lead particle size of emissions from baghouses was reported to be one micron or less, while those from concentrate storage ranged upward to 100 microns.

## PRIMARY COPPER

In the United States the smelting of copper concentrates includes the processing steps of roasting, reverberatory furnacing, and converting. Copper sulfide is the principal constituent of the ores and concentrates that are processed; however, lesser quantities of lead sulfide and other minerals are present. Lead emissions, therefore, may be expected during copper smelting.

Roasting removes volatile impurities and oxidizes sulfur. The reverberatory furnacing reduces copper and iron to form copper matte. Next, the matte is placed in the converter to remove the iron as iron oxide and as iron silicate slag. After the slag is poured off, the remaining sulfur is oxidized and blister copper remains. During these processing steps, oxides of sulfur, dusts, and fume are released from the concentrates. Particulate emissions from roasters are about 170 pounds per ton of copper produced and those from converters average near 240 pounds per ton  $\frac{1}{2}$ .

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1- McKee, Arthur G. & Co.; "Systems Study for Control of Emissions Primary Nonferrous Smelting Industry"; for NAPCA; June, 1969.

The following estimate for lead emissions from copper smelting has been prepared.

- 1 - Approximately 6 million tons of copper concentrates were processed in the United States during 1970 1/.
- 2 - The weighted average of lead in copper concentrates is about 2,130 ppm 2/.
- 3 - The quantity of lead contained in copper concentrates smelted during 1970 is calculated to be 12,780 tons.

$$6,000,000 \times \frac{2,130}{1,000,000} = 12,780$$

- 4 - Based on the assumption that 10 percent of the lead in the concentrates is lost in slags, solid wastes, and products during processing, the atmospheric emissions for 1970 (uncontrolled) are estimated at 11,500 tons.

$$12,780 - 0.1(12,780) = 11,500$$

- 5 - Based on an overall collection efficiency for lead of 85 percent, the estimated emissions for 1970 (controlled) were 1,700 tons.

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1- Minerals Yearbook; Bureau of Mines; Copper 1970 Preprint.

2- Information obtained concerning EPA analyses of 48 samples representing 5.6 million tons of copper concentrates.

## PRIMARY ZINC

In the United States there are three types of processing plants where primary zinc is recovered from ores, concentrates, fume, flue dust, and residues. They are the horizontal-retort and vertical-retort distillation facilities, and the electrolytic plants.

The major processing steps at the horizontal-retort facilities include roasting, sintering, and distillation. The operations are essentially the same at the vertical-retort plants, except for the distillation step which is carried out in vertical units. At the electrolytic plants the processing is somewhat different. It starts with roasting and is followed by leaching, purification, and electrolysis.

Zinc sulfide is the principal constituent of the raw materials that are processed at the plants; however, lesser quantities of lead sulfide and other minerals are present. Since lead is in the raw material, lead emissions to the atmosphere may be expected from all sources that emit dust and fumes. The roasting, sintering, and distillation steps are probably the sources of most plant emissions; however, unloading, storing, and conveying operations are responsible for substantial

emissions.

In the literature there are numerous references to emissions of metallic fume that occur in connection with roasting, sintering, and distillation. It has been reported that gases released from sintering contain lead fume that is approximately 11 percent lead by weight <sup>1</sup>/<sub>1</sub>. Another reference indicates that dust released from sintering is in the order of 250 pounds per ton of zinc produced <sup>2</sup>/<sub>1</sub>. This information, coupled with production figures from the U. S. Bureau of Mines, indicates lead emissions due to sintering operations in 1970 were in the order of 100 tons. Unfortunately, there is not sufficient information available to accurately estimate lead emissions from roasting, distillation, and fugitive sources.

As an alternative, the following estimate has been prepared.

- 1 - Approximately 1.5 million tons of zinc ores and concentrates were smelted in the United States

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1- Johnson, G. A., Lund, R. E., and Peterson, K. F.; "Air Pollution Prevention at a Modern Zinc Smelter"; Air Repair; 3(3); Feb., 1954.

2- McKee, Arthur G. & Co.; "Systems Study for Control of Emissions Primary Nonferrous Smelting Industry"; for NAPCA; June, 1969.

during 1970 1/.

2 - The average lead content of zinc concentrates is about 6,000 ppm 2/.

3 - The quantity of lead contained in zinc ores and concentrates smelted during 1970 is calculated to be 9,000 tons.

$$1,500,000 \times \frac{6,000}{1,000,000} = 9,000$$

4 - The estimated lead content of the primary zinc produced during 1970 is 3,200 tons.

<u>Grade</u>	<u>Production</u> Tons <u>1/</u>	<u>Lead</u> <u>Content</u> <u>3/</u> %	<u>Lead</u> Tons
Special high	370,000	0.003	11
High	100,000	0.07	70
Intermediate	48,000	0.2	96
Brass special	66,000	0.6	396
Prime western	294,000	1.6	<u>4,704</u>
			5,277

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1- Minerals Yearbook; Bureau of Mines; Zinc 1970 Preprint.

2- Information obtained concerning EPA analyses of 62 zinc concentrate samples.

3- A. S. T. M. Specification B6-62T for primary slab zinc.



Estimated lead content assumed to be 60 percent of the maximum allowable.

$$5,277 \times 0.6 = 3,200$$

- 5 - Based on the assumption that 10 percent of the lead in the ores and concentrates is lost in slags and solid wastes during processing, the atmospheric emissions for 1970 (uncontrolled) are estimated at 4,900 tons.

$$9,000 - 0.1(9,000) = 3,200 - 4,900$$

- 6 - Based on an overall collection efficiency for lead of 95 percent, the estimated emissions for 1970 (controlled) were 240 tons.

## SECONDARY LEAD

In the United States secondary lead production is an important factor in the total lead supply. During 1970 it was nearly equal to the production of primary lead. For the years 1966 through 1970 the U. S. Bureau of Mines reported the amount of lead produced from scrap to be about 43 percent of the quantity consumed. During that four-year period domestic consumption increased only 2.8 percent, while secondary production increased 4.3 percent.

The larger portion of the raw material supply for the secondary lead industry is "old scrap" reclaimed from discarded end use products such as storage batteries, type metal, bab-bitt, lead-covered cable, and various items that contain solder. During 1970 old storage battery lead plates accounted for 65 percent of the total scrap consumed and the quantity of "new scrap", consisting of drosses and residues, was nearly 16 percent.

The equipment and facilities for processing secondary lead range from sweating furnaces and small remelting pots to complex smelting and refining operations similar to those

in the primary lead industry. The products produced are antimonial lead, refined pig lead, solder, type metals, bab-bitt, cable lead, and miscellaneous alloys. The most important consumer of secondary lead is the storage battery industry.

The operations performed at secondary lead plants are many and varied. At the larger facilities where reverberatory, blast, and pot furnaces are employed, nearly any type of scrap may be used and many different products can be produced. The grade of product desired determines the type of equipment to be used and the scrap materials for the charge. Hard lead, which typically contains from 5 to 12 percent antimony, is made in the blast furnace. Semisoft lead is a product of the reverberatory furnace and it normally contains not more than 0.3 to 0.4 percent antimony. Soft or high-purity lead is the metal obtained after semisoft lead has been refined in the pot furnace.

The typical practice at larger plants is to treat the scrap material in a reverberatory furnace to produce a crude semisoft lead and a leady slag. The charges, which are made up of a mixture of materials such as battery plates, drosses, residues, and lead scrap, are added intermittently

to the furnace to maintain a small mound of unmelted material on top of the bath. Then as the level of the molten metal rises, the product is tapped off.

The reverberatory furnace is fired with gas or oil and the temperature is maintained at approximately 2,300 F. The smoke and fumes produced include oxides, sulfides, and sulfates of lead, tin, arsenic, copper, and antimony. It has been reported that smoke and fumes are equal to approximately 7 percent of the charge, slag about 46 percent, and metal recovery 47 percent 1/. The same report shows the results of a reverberatory test run conducted while processing battery groups at a rate of 2,500 pounds per hour. The dust and fume emission at the furnace outlet was 130.5 pounds per hour, or 104 pounds per ton of process weight. With an assumed metal recovery of 47 percent, the dust and fume emission was 222 pounds per ton of product. Another report indicates that dust and fume from a reverberatory furnace is approximately 225 pounds per ton of metal reclaimed 2/.

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1- Danielson, J. A.; "Air Pollution Engineering Manual"; PHS Publ. No. 999-AP-40; 1967.

2- McKee, Arthur G. & Co.; "Systems Study for Control of Emissions Primary Nonferrous Smelting Industry"; for NAPCA; June, 1969.

The leady slag from the reverberatory is further processed in a blast furnace. It is part of the usual charge which also includes miscellaneous drosses, oxides, scrap cast iron, coke, limestone, and rerun blast furnace slag. The coke is the source of heat and the combustion air that is required is introduced through tuyeres located near the bottom of the furnace. As the gases pass upward through the charge they carry bits of coke fuel, oxides, and other particulates. Approximately 70 percent of the molten material is the product, hard or antimonial lead, and 30 percent is slag.

The results of a blast furnace test run show 229 pounds per hour dust and fume emission at the furnace outlet while processing 2,670 pounds per hour of battery groups, dross, and slag <sup>1</sup>/<sub>1</sub>. Based on the antimonial lead produced, the particulate emission was approximately 268 pounds per ton of product.

After the production of semisoft and hard lead in reverberatory and blast furnaces, further processing is often required and pot furnaces may be used for this purpose. One of the

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1- Danielson, J. A.; "Air Pollution Engineering Manual"; PHS Publ. No. 999-AP-40; 1967.

refining operations most commonly employed is removal of copper and antimony to produce soft lead. Normally, the semisoft lead from the reverberatory furnace is transferred in a molten state to a pot furnace where the temperature is allowed to drop to about 620 F. Sulfur is added, the mixture is agitated, and copper sulfide is skimmed off as a dross. When aluminum is added it reacts preferentially with copper, antimony, and nickel to form compounds that can be skimmed from the surface of the liquid. The antimony may also be reduced by bubbling air through the molten lead.

Pot furnaces are also used extensively for alloying operations. When commencing with a metal that contains less alloying elements than desired, the required amounts of each are calculated and the proper quantities added to the melt. Operating temperatures are usually not more than 750 to 900 F and emissions are relatively low. Uncontrolled emissions of particulate have been reported to average 0.8 pound per ton processed 1/.

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1- "Compilation of Air Pollutant Emission Factors (Revised)"; U. S. Environmental Protection Agency; Research Triangle Park, N. C.; Office of Air Programs; Publ. No. AP-42; Feb., 1972.

Lead recovery operations other than those described also add to the air pollution problem. Two of the most common are: (1) the sweating of lead and solder from scrap; and, (2) the incineration of lead-covered cable. Emissions from both these processes vary considerably due to the composition and condition of the scrap material.

While this study was in progress all of the large producers of secondary lead and numerous local air pollution agencies were contacted to obtain data regarding lead production, air pollution control equipment, magnitude of emissions, and other related information. Emission data was available concerning 29 plants that produced nearly 90 percent of the secondary lead during 1970. The reports, which were principally from industry, showed that lead emissions to the atmosphere averaged 0.7 pound per ton of lead produced.

In addition to the information reported by industry, results were available showing the lead content of particulate obtained during five stack tests conducted during the period November, 1971 through February, 1972 <sup>1</sup>/. Two reverberatory and

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1- Source Test Nos. 71-CI-29; 71-CI-33; 71-CI-34; 72-CI-7; and 72-CI-8.

three blast furnace stacks were sampled. Lead emissions from the reverberatories were 0.03 and 0.04 pound per ton of lead processed, while those from the blast furnaces were 0.009, 0.024, and 0.08 pound per ton.

Industry reports of lead emissions from two plants were essentially the same as the lead emissions calculated from test results. At another plant, however, the lead emissions were 0.04 pound per ton according to test data, while the industry report was 0.26 pound per ton. It was subsequently confirmed that this industry report included all plant emissions and not just the stack emissions from the reverberatory furnace.

Based on the information obtained from industry, lead emissions to the atmosphere due to the production of secondary lead totaled 220 tons during 1970. There were 13 secondary plants where lead emissions were more than 20 pounds per day.



## LEAD OXIDE

Lead has two simple oxides, litharge ( $\text{PbO}$ ) and lead dioxide ( $\text{PbO}_2$ ), and a mixed oxide, red lead ( $\text{Pb}_3\text{O}_4$ ). Of these, litharge and red lead are the most important. Litharge is a high-tonnage, heavy chemical prepared by various processes for a variety of specific uses including storage batteries and pigments. The commercial product varies in color from reddish-brown to grayish-black to bright yellow. Red lead is prepared from lead monoxide and is added to paints for its rust-inhibiting properties. It also finds some use in storage battery plate pastes, but the partially oxidized black powder, black oxide, or battery oxide, is most widely used for this purpose. Usually the black oxide used in storage batteries is a mixture of about 60 to 80 percent lead monoxide, the remainder being finely divided metallic lead. It is quite distinct from the usual litharge available on the market.

Lead dioxide is an oxidizing agent in the manufacture of dyes, chemicals, matches, pyrotechnics, and rubber substitutes. It is also used as a curing agent for liquid polysulfide polymers, converting them to rubbers at room temperature without shrinkage.

The commercial manufacture of lead monoxide is based on furnace techniques. There are four principal methods in use: (1) metallic lead is partially oxidized and milled to a powder which is charged into a reverberatory furnace at about 1,100 F to complete the oxidation to ordinary "chemical" litharge; (2) pig lead is oxidized and stirred in a reverberatory furnace or rotary kiln directly to lead monoxide; (3) molten lead is run into a cupelling furnace held at about 1,800 F and molten litharge is produced; and, (4) molten lead at about 950 F is atomized into a flame where it burns vigorously, producing "sublimed" or "fumed" litharge. In all cases, the product must be cooled quickly to below 570 F to avoid formation of red lead.

The litharge used in battery pastes is usually a mixture of lead oxide and a finely divided metallic lead, variously known as gray oxide or black oxide depending on the amount of lead it contains. The litharge-lead mixture is manufactured by the ball mill process or the Barton process. Using the ball mill, the pieces or balls of pure lead are oxidized by the frictional heat generated from the tumbling of the lead in the mill. This oxidation reaction is exothermic and the heat generated accelerates it further. During the action the lead

oxide that forms on the surface of the lead balls is removed and ground. This mixture usually approximates 70 percent lead oxide to 30 percent unoxidized finely divided lead. Ball mill oxides give batteries long life and good capacity, but they are being superseded by Barton oxides. The Barton process depends on the oxidation of lead in the molten state. Molten lead is fed into a circular pot and rapidly stirred. A series of baffles within the pot atomize the lead, breaking it into extremely small droplets. An air stream in the pot oxidizes these small droplets, and the material is carried by the air stream to a collecting system.

Commercial red lead is composed principally of trilead tetroxide,  $Pb_3O_4$ , and smaller amounts of lead monoxide. The manufacture of red lead begins with litharge which is charged into a reverberatory furnace, where it is held at a temperature of 900 to 950 F while air passes over. The process consists of oxidation until the desired level of red lead is obtained. An 85 percent grade red lead is usually completed in about 24 hours but a longer time is required for grades containing a higher percentage of true red lead. Following cooling, the material is ground to required particle size.

Lead dioxide is a brown powder which decomposes rather easily to lower oxides, releasing oxygen when heated to 555 F. It is commercially produced by the treatment of an alkaline red lead slurry with chlorine, but may also be produced by anodic oxidation of solutions of lead salts. In this case a strong oxidizing agent such as hydrogen peroxide or chlorine gas is added to the solution to obtain the lead dioxide.

Production reports for 1970 reveal that nearly 78 percent of the 400,707 tons of lead oxide produced in the United States was used in storage batteries <sup>1</sup>/<sub>1</sub>. Another 19 percent was used in the form of red lead and litharge in the manufacture of pigments. Most of the oxide was processed at battery plants or at the secondary lead plants.

Information obtained from companies that currently produce about 60 percent of the lead oxide indicates that lead emissions from baghouses range from 0.2 to 2.8 pounds per ton processed <sup>2</sup>/<sub>1</sub>. During 1970 the lead emissions from lead oxide plants averaged 0.7 pound per ton of lead processed.

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

2- Private communication.

Lead emissions to the atmosphere due to the manufacture of lead oxide totaled 140 tons during 1970. There were 16 plants producing lead oxide where lead emissions were more than 20 pounds per day.

### CONSUMER PRODUCT MANUFACTURING

In the United States during 1970 nearly 70 percent of the primary and secondary lead was used in metal products, including storage batteries, ammunition, solder, cable covering, type metal, brass and bronze, bearing metals, caulking lead, sheet lead, pipe and fittings, collapsible tubes, foil, casting metals, and terne metal. Approximately 20 percent was used in gasoline antiknock additives and miscellaneous chemicals. The remainder was used in pigments and for other miscellaneous purposes.

The largest quantity of lead was consumed in the manufacture of storage batteries, principally for motor vehicles.

## STORAGE BATTERIES

The largest single use of lead in the United States is in the manufacture of lead-acid storage batteries, which are the type of batteries found in automobiles, motor trucks, mine locomotives, golf carts, industrial trucks, emergency lighting systems, telephone networks, and numerous other applications. During 1970, nearly 44 percent of the total lead supply was used for this purpose. From the standpoint of lead emissions to the atmosphere, the battery manufacturing industry is important because many factories are located in densely populated areas. There is a large emission potential from each, even from the relatively small plants.

The installations in which storage batteries are manufactured vary considerably in size and in the type of operations performed. Some of the larger plants make their own lead oxide and some operate secondary lead recovery facilities. Some plants produce less than 50 batteries per day, while others produce more than 12,000 per day. The quantity of lead and lead oxide used each day may be less than 500 pounds or more than 300,000 pounds. At a large plant, without air pollution controls, the lead emissions to the atmosphere

could be several tons per day.

A lead-acid storage battery consists of positive and negative plates, separators, an electrolyte of dilute sulfuric acid, and a case. Both wet- and dry-charged batteries are produced and the general operations in the manufacturing process are shown in Figure IV. The plates are made up of a structural member called the grid and lead oxide paste. The grid, which is inactive, provides mechanical support for the active portion and a conductive path for the electric current. These perforated grids are generally cast from lead hardened by the addition of between 6 and 12 percent antimony, including small amounts of arsenic and tin. Hard lead is the term applied to the most common alloys used in storage battery construction. A typical analysis of hard lead is as follows: antimony, 7 percent; tin, 0.25 percent; arsenic, 0.1 percent; and lead, 92.65 percent.

Casting techniques for grids vary with the alloy used, the type of molds, and the mold preparation before casting. Highly efficient casting machines have been developed for gravity-casting of grids. A molten lead alloy is poured into iron grid molds at about 900 F where it is allowed to freeze.



# STORAGE BATTERY MANUFACTURE FLOW DIAGRAM

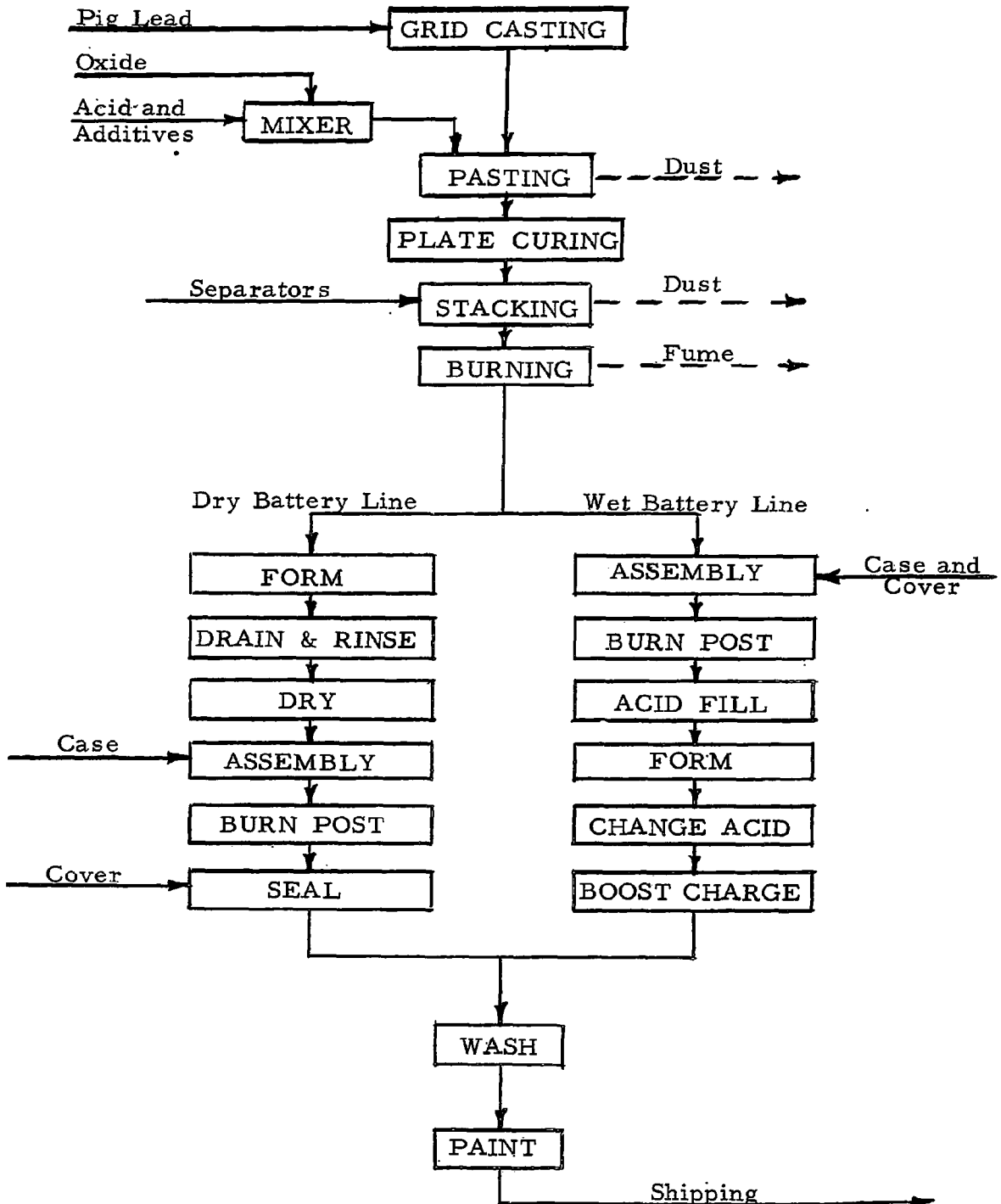


Figure IV

When the grids are ejected from the molds they can be hardened by quenching or spraying with cold water prior to trimming and stacking.

Typically, the lead oxide paste is made by adding water to lead oxide in a mixer and blending to form a stiff paste. Dilute sulfuric acid is then added slowly with constant mixing and cooling until the desired consistency and density are attained. Three types of mixers are used; they are known as the muller type, the dough type, and the day type. The muller-type mixers are most common especially for batch sizes from 1,200 to 2,400 pounds. Mixers should be water-jacketed and air-cooled to prevent excessive temperatures which cause the paste to become stiff and difficult to apply to the grids. Pastes for both positive and negative plates are made similarly except that so-called "expanders" are added to negative pastes to serve as an aid in activating these plates at low temperatures and high rates of discharge.

Following the preparation of the paste, machines are used to force it into the interstices of the grid structure. Then there is a short drying period and a curing step prior to the stacking and burning operations. Curing is a process tha

increases the strength of the plates. Stacking is the procedure of assembling the cured plates and their separators into elements. Burning is the term applied to the operation of melting lead to weld the plates together. The negative plates are joined by burning to form one electrode, and the positive plates are joined together likewise to form the other. The welded elements can go either to the dry battery line or the wet battery line.

In the dry battery line, the element stacks are placed in containers filled with acid and connections are made for the forming process, which is a charging operation that converts the paste to sponge lead in the negative plate and to lead peroxide in the positive plate. During this process, which requires several hours, the sulfuric acid becomes slightly more concentrated. After the element has been formed it is removed from the container, permitted to drain for a very short period, rinsed by moving countercurrent through fresh water, and placed in an oven to dry. The dried elements are assembled in a battery case, the posts are welded in place, and the cover sealed to the case. The completed battery is then ready for washing, painting, and shipping.

The welded assembled elements can also be used to produce the wet battery. In this instance the elements are placed in a battery case, the posts burned, and the battery filled with acid. These batteries undergo the same forming process as the dry batteries, after which the acid is dumped. Fresh acid is then added and the battery is given a boost charge prior to washing, painting, and shipping.

The above is a brief description of the principal operations involved in lead-acid storage battery manufacture. There are, however, many minor process variations in all of the plants that were visited during this study.

Nearly all steps in storage battery manufacturing employ the use of lead and have a potential for lead emissions; however, only the principal emission sources are indicated in Figure IV. During melting and casting operations, the temperature of the molten lead is usually below 900 F and the degree of fuming is not significant. In many plants hoods have been installed over the melting pots for protection of personnel, and the fumes are discharged directly to the atmosphere without passing through dust collecting devices.

In this report the manufacture of lead oxide has been discussed

separately. Even though many large battery manufacturers prepare this material in their own plants, it must be handled in much the same manner as purchased oxide. Usually it must be moved, stored, and moved again before it enters the weigh bins and paste mixers. Each time it is handled a considerable amount of dusting occurs and care is required to avoid the release of dust to the atmosphere. Normally, the storage and handling systems are enclosed and connected to weigh bins and paste mixers through dust-tight seals. Bag filters and cyclone collectors are commonly employed to remove dust from the air that is discharged from the equipment.

After the damp lead oxide paste has been prepared, the emissions are relatively insignificant until the pasted plates have been dried. Then there is more dusting as the plates are handled and stacked. During burning or welding of the assembled elements, fuming is the problem. It is common practice for the operators to wear protective masks at stacking and burning stations. It is also common practice to install hoods and exhaust dust systems for removal of pollutants from these areas.

According to the information obtained during this study, more bag filters are employed for air pollution control in battery plants than any other type of dust collecting equipment. Cyclone collectors with water sprays are also popular and are sometimes used in series with bag filters. The data received from 55 plants, employing about 11,000 persons and producing approximately 75 percent of the storage batteries, indicates that lead emissions to the atmosphere due to battery manufacture totaled 480 tons during 1970. Lead emissions from plants with air pollution controls averaged 1.3 pounds per ton of lead processed, while those from plants without controls were about 8 pounds per ton. It is estimated that there are 24 battery plants where lead emissions to the atmosphere exceed 20 pounds per day.

## GASOLINE ADDITIVES

In the United States the second largest use of lead is in the manufacture of the lead alkyls, tetraethyl lead (TEL) and tetramethyl lead (TML), which constitute practically all of the gasoline antiknock agents in use today. During 1970 approximately 20 percent of the total lead supply was used for this purpose.

From the standpoint of lead emissions to the atmosphere, the manufacture of TEL and TML is important. Their volatility is relatively high and emissions are difficult to control because they occur primarily in vapor form.

Although some lead alkyls are manufactured by an electrolytic method, 90 percent or more are produced in a sodium-lead alloy process in either batch or continuous reactors. In the batch process tetraethyl lead is made by the reaction of ethyl chloride with a sodium-lead alloy, according to the equation  $4 \text{ NaPb} + 4 \text{ C}_2\text{H}_5\text{Cl} \longrightarrow \text{Pb}(\text{C}_2\text{H}_5)_4 + 3 \text{ Pb} + 4 \text{ NaCl}$ .

Following the completion of the reaction, the product is

chloride. Then ethylene dichloride, ethylene dibromide, and dyes are combined with the product to form the finished additive.

The first step in tetraethyl lead production (see Figure V) is the making of the sodium-lead alloy. Lead, which may be virgin and recycle, is melted and mixed with sodium in a melt pot in a ratio of 90 parts lead to 10 parts sodium. This produces a lead-sodium alloy which is flaked, then loaded into hoppers under a blanket of nitrogen to be taken and dumped into horizontal autoclaves.

After the alloy is in the autoclaves, the ethyl chloride is fed over a period of several hours. The reaction takes place during the ethyl chloride feed time and an additional 30 to 60 minute cook period. The temperature in the autoclave is maintained at about 160 to 165 F and by-product gases are vented throughout the reaction. Finally, the autoclaves are vented of excess ethyl chloride and the reaction mass is discharged into steam stills containing water.

In the still operation, the remaining dissolved ethyl chloride is removed with steam followed by steam distillation of the TEL from the residual mixture of lead metal and sodium chloride. Steam is passed through the still for about two



TEL BATCH PLANT FLOW DIAGRAM  
SODIUM-LEAD ALLOY PROCESS

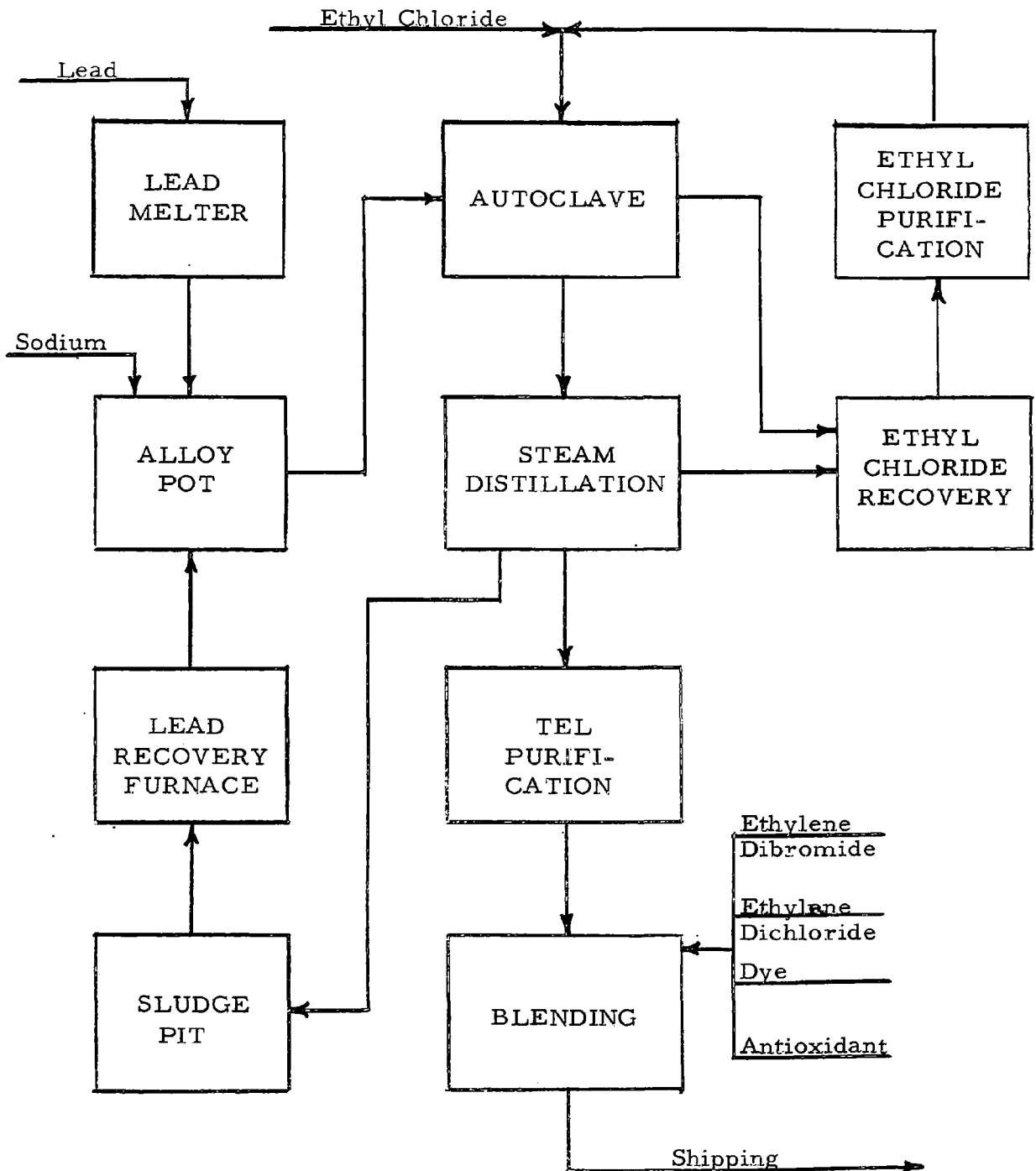


Figure V

hours while the mass is agitated.

Following steam distillation, the crude TEL is purified by air blowing or washing with dilute aqueous solutions of oxidizing agents such as hydrogen peroxide in order to remove small amounts of organometallic compounds of other metals. Then the tetraethyl lead is washed with water and separated, and is ready for blending into antiknock fluids.

Residue from the steam-still distillation is dropped into a sludge pit. Sodium chloride is washed from the residue and the remaining lead metal sludge is dried, purified by smelting, and recycled into the sodium-lead alloy manufacture. This is a very important step as less than 25 percent of the lead in the alloy is converted to tetraethyl lead on one pass; thus, a large amount of metallic lead remains in the residue. For every pound of lead in tetraethyl lead, four and one-half times that amount must be handled in the process.

The antiknock fluid is completed by mixing the following in a blender: tetraethyl lead, halogen compound, an identifying dye, antioxidant, and a surface ignition control compound. Finally it is pumped through bag filters into tank cars or bulk-storage tanks ready for shipment.

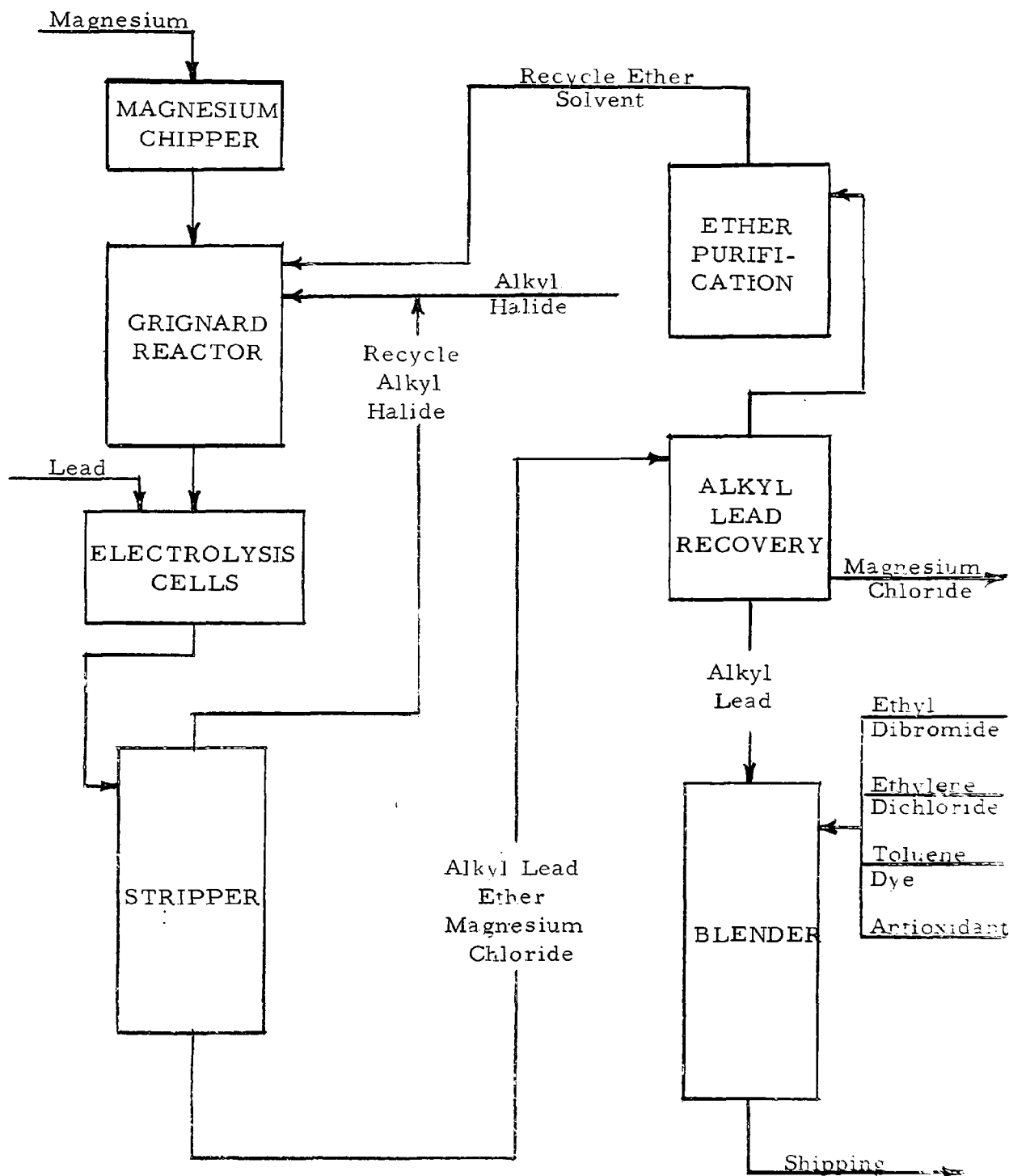
The continuous process for the manufacture of TEL is an adaptation of the batch process. The principal steps are essentially the same, except a continuous reactor is used instead of autoclaves and product separation operations vary somewhat.

Tetramethyl lead is manufactured by a batch process similar to that described for TEL. The essential difference is that methyl chloride is used instead of ethyl chloride, aluminum chloride is used as a catalyst, and higher operating temperatures and pressures are required for the TML synthesis.

The electrolytic process for making TEL and TML is based on the fact that organomagnesium halides ionize in ether solvents and these solutions can be electrolyzed. It is claimed the process has two advantages over other methods. First, the electrolytic process is more versatile and various alkyl lead compounds can be produced without major modification to the equipment. Second, inefficient recycling of metallic lead is avoided since this by-product is not formed in the reaction.

The first step in the electrolytic process (see Figure VI) is the batch preparation of the alkylmagnesium halide. The

# TEL-TML PLANT FLOW DIAGRAM ELECTROLYTIC PROCESS



reactants are magnesium chips and alkyl halide. The solvent is a mixture of ethers. The reactants plus the solvent are fed into Grignard reactors. The reaction is exothermic and is carried out at low pressure (10 to 20 p.s.i.g.) and a temperature of about 100 F. The resulting alkylmagnesium halide and ether solvent is metered into the electrolysis cells where lead pellets are used as the anode and steel walls as the cathode. After electrolysis, the solution contains alkyl lead, ether solvent, alkyl halide, and magnesium chloride. First, the alkyl halide is stripped from the solution, then the other three compounds are separated by distillation and solvent extraction. The resulting alkyl lead is fed into a blender where other ingredients are added to produce the final product.

While this study was in progress, information was obtained from industry regarding the magnitude and nature of lead emissions, manufacturing operations, and air pollution control equipment. Part of the lead emissions are in vapor form and part are particulates composed of lead carbonate, lead chloride, and lead oxide. The vapors, when emitted, are TEL and TML, but they are soon converted to lead oxide after exposure to the atmosphere. One lead alkyl

manufacturer has reported that electron micrographs indicate particulates range in size from 0.01 to 2 microns, but are generally below 0.5 micron.

High-energy venturi scrubbers and cyclones with water sprays are the types of equipment most often used to control particulate emissions. Refrigeration systems are used to lower the temperatures and reduce vapor emissions.

The information obtained from industry indicates that lead emissions to the atmosphere due to the manufacture of lead alkyls totaled 1,900 tons during 1970. Lead emissions ranged from 0.8 to 29 pounds per ton of lead used, averaging 13.6 pounds per ton, and they exceeded 20 pounds per day at each of the six manufacturing plants.

## PIGMENTS

The use of lead in pigments and paints is still important even though the quantity used for this purpose has decreased substantially during recent years. Basic carbonate white lead, basic lead sulfate, leaded zinc oxide, and certain lead silicates are employed in some outside paints. Red lead or "blue" basic lead sulfate may be an addition in primers and metal protective paints. Lead also produces certain colored pigments, notably the lead chromates. Most of the yellows, greens, and reds are lead chromates, either alone or precipitated with other pigments. Leaded pigments may be used as artists' colors or in printing inks, and yellow shades are rapidly growing as traffic marking paints.

Basic carbonate white lead is one of the oldest pigments used in paints. Because of its basic qualities, white lead undergoes a reaction with linseed oil fatty acids which makes it useful in conjunction with other lead pigments, zinc oxide, titanium dioxide, and extenders for the manufacture of ready-mixed oil paints. The lead reaction imparts adhesion, toughness, elasticity, and improves durability. Films pigmented with basic carbonate white lead weather in such a manner

that the paint film is maintained in good condition for repainting without extensive preparation.

There are several processes for manufacturing basic carbonate white lead. They all make use of the reaction of lead or litharge ( $\text{PbO}$ ) with acetic acid to produce lead acetate, which is then reacted with carbon dioxide to form basic carbonate white lead.

Basic sulfate white lead imparts to oil paint films the properties of adhesion, elasticity, toughness, and durability. However, it is not satisfactory as the sole pigment in pure white lead paint and is used in conjunction with other pigments in exterior oil paints. It may be prepared by chemical or fume processes. The chemical process begins with finely divided lead or a mixture of lead and litharge suspended in water. Sulfuric acid is then added to produce a precipitate of basic sulfate white lead which is filtered off, dried, ground, and bagged. The fume processes use baghouse collection. In one method lead sulfate, or galena, is heated in an oxidizing atmosphere, but another procedure uses a spray of molten lead which is reacted with sulfur dioxide obtained by burning sulfur. Both processes produce a fume of basic sulfate



white lead which is converted to a fine powder by cooling and then collected.

Basic silicate white lead with characteristics similar to basic carbonate white lead is a pigment useful in paints used to cover redwood or cedar siding as it inhibits discoloration caused by the natural dyes in these woods. This pigment is prepared by a dry-phase reaction in which proper proportions of silica, lead oxide, and basic lead sulfate are heated together.

Leaded zinc oxides may also be used as a pigment in exterior finish coat oil-base house paints as it is a convenient means of introducing both lead and zinc into the formula. These oxides contain basic sulfate white lead. They may be produced either by smelting and fuming combinations of zinc and lead sulfide ores, or by mechanically blending fractions of zinc oxide and basic lead sulfate which have been prepared separately.

An important family of yellow and orange inorganic pigments results from the characteristic medium yellow color of normal lead chromate. A wide range of closely related yellow and orange pigments is produced, from light greenish-yellow

shades to extra deep orange shades. The chromes in general combine brilliance of color and great staining power with considerable hiding power. They are reasonably stable and retain their color even in impure air, although they are not absolutely fast to light, gradually fading on exposure. Another desirable property is their ability to inhibit the corrosion of metals. Thus, they are efficient as primers.

All chrome yellows are precipitates which are formed in tanks equipped with agitators. The precipitates are washed to remove soluble compounds, filtered, dried at temperatures not above 200 F, and ground. Raw materials for the production of chrome yellows are numerous and varied.

They include litharge or lead carbonate, sodium bichromate, acids such as nitric, acetic, sulfuric, or hydrochloric, and various alkalies. If litharge, nitric acid, and sodium bichromate are used the litharge and nitric acid combine to form lead nitrate and water. When sodium bichromate is added, the result is lead chromate, sodium nitrate, and nitric acid. This produces a medium yellow.

The primrose and lemon shades of chrome yellow differ from the medium yellows in composition in that substantial

amounts of lead sulfate or other lead compounds are present with the normal lead chromate. The process of manufacture is generally the same as that for the medium yellows, except that a part of the sodium bichromate is replaced by sulfuric acid. Many variations in shade may be obtained by controlling the exact percentage combination of lead chromate and lead sulfate.

The chrome yellows and oranges have relative low cost and good qualities which make them useful pigments in paints, lacquers, traffic-line paints, printing inks, papers, linoleum, and leather finishes.

All chrome oranges contain basic lead chromate, which is present in increasing proportion to the normal lead chromate to obtain the desired color. The more completely the orange chrome is converted to the basic compounds, the deeper the shade of reddish-orange produced. Manufacturing equipment and processes are generally similar to those used for making chrome yellow. The chrome oranges are more resistant to alkalies and less resistant to acids than the yellows. Their larger crystals give them improved light-fastness but lower hiding power. One specific bright

red-orange shade of basic lead chromate is used for airport markings.

Related to the basic lead chromates is basic lead silicochromate. Basic lead chromate is deposited on the surface of a core of silica. During manufacture the lead chromate-silica composite is subjected to calcination conditions to bond the chromate coating to the silica, converting part of the basic lead to basic lead silicate. This pigment is widely used in primers for ferrous metals. When exposed to weather it does not undergo carbonation as does the pigment red lead. Metal primed using basic lead silicochromate may be stored in the field for extended periods without rapid weather deterioration. The pigment may also be used in intermediate and finish coats of paint for steel structures to provide additional protection against corrosion.

Chrome greens are some of the most widely used pigments. They find wide application in many kinds of paints such as house paints, sash and trim paints, enamels (both air-drying and baking), lacquers, and flat paints; they are also used in printing inks, calcimines, oilcloth, and paper. The pigments include a wide variety of hues from extra-light yellow

green to an extra-dark green. These greens are all intimate mixtures of chrome yellows and iron blues. Since these pigments are composites, their compositions depend on the proportions of chrome yellow and iron blue. Variations in hue may also be produced by the shade that is used, which is a redder yellow producing a more olive green.

The mixtures that produce chrome greens may be made by blending fresh wet precipitates, by blending the dry powders, or by causing the chrome yellow precipitate to form on already prepared and washed iron blue. Manufacture requires the same equipment as needed for the chrome yellows: tanks for solution, precipitation, and washing; filters; driers; and pulverizers.

Another group of oranges using lead are the molybdenum oranges which are more brilliant than the chrome oranges. These oranges are characterized by strong color, high hiding power, and high tinting strength. They are used in many kinds of paints, enamels, and lacquers. Use is also made in floor coverings and printing inks. These pigment colors result from the coprecipitation of lead chromate and lead molybdate, often in the presence of lead sulfate. Lead

molybdate is a white compound; the coprecipitation of lead chromate and lead sulfate produces a light chrome yellow. Molybdenum oranges are produced in a wide range of composition, but a typical grade consists of 81 percent lead chromate and 11 percent lead molybdate.

Blue basic lead sulfate is another lead pigment sulfate known as blue lead and sublimed blue lead. It is a dark slate-gray color pigment used chiefly in primers and finish coat paints for structural metal. Blue lead is manufactured by feeding a mixture of lead ore and coal or coke into a Scotch-hearth furnace. The lead sulfide in the ore is partially oxidized to lead sulfate and lead oxide, which combine to form a fume of basic lead sulfate. Excess lead sulfide and carbon, lead sulfite, and zinc oxide also comprise a part of the fumes which are collected in baghouses.

Litharge and red lead are both oxides of lead. These oxides are important pigments and their preparation has already been discussed. Litharge was used almost exclusively until modern times. Red lead is now an alternative to litharge. Both oxides are used mainly in the preparation of boiled oil, varnishes, and liquid driers. Their activity as driers is

developed by heating with oil. When they combine with the oil, soluble lead soaps are formed. In addition, red lead is used as a pigment for paints to protect metal surfaces. It is a prime coat on massively exposed iron and steel structures such as bridges, ship hulls, water tanks, and fuel tanks. In combination with linseed oil, it forms tough elastic films with excellent adhesion to ferrous metals. Litharge is the usual starting point for the manufacture of other lead chemicals such as chrome pigments, basic lead carbonate, basic lead sulfate, basic lead silicate, lead arsenate, red lead, and lead soaps and greases.

Other pigments using lead include antimony yellow and cas-sel yellow which are used as artists' colors. Orange mineral is another color resulting from further oxidation of red lead. Calcium plumbate, a light yellowish-buff pigment, is made by heating lime and litharge at about 1,300 F. Flake powdered lead is sold as a powder or a paste for use as a pigment in primers on galvanized iron, stainless steel, lead, and light metals.

Paint manufacturing in the United States is an industry comprised of a few large companies and numerous small ones.

Currently there are more than 2,000 establishments that manufacture paint and about 150 that make pigments. The information obtained from industry for this report indicates that most pigment manufacturers use some type of air pollution control equipment, but that many of those mixing paint only have none. One large pigment company without controls has reported analyses which show that lead emissions average about 9.5 pounds per ton of lead contained in the product. Others using bag filters and scrubbers reported that lead emissions average 1.3 pounds per ton of lead used. Based on an average of 1.3 pounds per ton, lead emissions resulting from the manufacture of pigments are estimated by the Contractor at 63 tons for the year 1970. There are 6 pigment plants with lead emissions exceeding 20 pounds per day.

Reports from several large paint manufacturing establishments indicate that wet scrubbers and bag filters are the air pollution controls most often used in connection with paint mixing operations. Sometimes both types of equipment are used in the same plants. Lead emissions when using these controls have been reported to range from less than 1 to nearly 5 pounds per ton of lead processed, averaging 1.3 pounds per ton. When not controlled, emissions range from



less than 3 to more than 20 pounds per ton. Based on an average of 3 pounds per ton, lead emissions due to paint mixing during 1970 have been estimated by the Contractor at 147 tons.

## AMMUNITION

Lead's density has made it an ideal metal for bullets and shot, as it permits the attainment of a high momentum necessary for maximum striking power. Most of the lead shot manufactured goes into shells for sporting ammunition while the usual military applications are bullets and bullet cores for pistol, rifle, and machine gun.

The lead used in shot production is usually alloyed with arsenic and/or antimony. Additions of up to 1 percent arsenic increase fluidity and allow the formation of a perfect spherical shape. From 2 to 6 percent antimony in the alloy increases hardness for long-range loads.

The manufacture of shot is an example of casting without a mold. Casting takes place from the top of a tower or the upper part of a mining shaft. The height of the pouring floor is determined by the maximum size of the shot to be poured; the larger the shot to be made, the higher the pouring floor. The lead alloy in pasty form is put into a gas-heated iron pot, the base of which is perforated with a series of holes smaller than the shot desired. The bottom of the pan is covered with a sludge of oxidized lead so that the molten

metal will ooze slowly through and form round drops. During the stirring of the pasty metal, spheres of molten alloy flow through the sieve, break into individual drops, and fall to the lower end of the shaft where they are caught in a tank of water. During the fall the metal cools and solidifies into spherical shot. The water keeps the spheres from being flattened during landing.

After the shot is collected in the water it is dried, mixed with graphite to polish it, and then screened to eliminate odd sizes. Next, the shot is rolled down sloping glass tables which have a narrow trough at the bottom edge. Perfectly round shot gather enough momentum during rolling to leap the trough, but misshapen shot fall into the trough for subsequent remelting. Grading operations are repeated several times. Then the shot is loaded into shells and becomes ready for use.

For bullet cores, lead is usually extruded as wire, which is cut to length and swaged to the approximate shape of the bullet. The size and shape of the cores vary depending upon the type of bullet. In "ball" cartridges the entire core is lead alloy, but in tracer or incendiary cartridges, the lead core

is somewhat shorter than the jacket, the remaining space being filled with the tracer or incendiary chemicals.

Lead azide is an initial detonating agent used in commercial blasting caps and military ammunition. It is preferable to mercury fulminate with respect to stability, cost, and availability of raw materials. Lead azide is practically insoluble in most common solvents, is less sensitive to heat, impact, and friction than mercury fulminate, and overcomes a lower rate of detonation to be a superior initiator of detonation.

The compound may be produced in crystalline, colloidal, or dextrinated forms. The preparation of each form calls for a chemical reaction of sodium azide with lead nitrate or lead acetate in solution. Precipitated lead azide is then washed and stored under water. Any by-product liquor can be treated with soda ash to precipitate lead as lead carbonate.

The data presented in this study was obtained from establishments that consume about 35 percent of the lead used in the manufacture of ammunition. These companies have reported that their operations include lead casting, shot dropping, extrusion, slug forming, and tumble polishing, as well

as the manufacture of priming mixtures. Air pollution control equipment consists of bag filters for tumble polishing operations only. According to recent stack tests conducted by one ammunition manufacturer, lead emissions to the atmosphere are less than one pound per thousand tons of lead processed. Based on the data reported, lead emissions due to the manufacture of ammunition are considered to be negligible.

## SOLDER

Due to the wide variety of soldering procedures in use today, there is a great demand for solder in various forms. Solder can be obtained as wire or tape in a continuous length on a spool or shaped and cut into "preforms" such as rings, washers, discs, or pellets. It may also be purchased as bars, wire, or pellets for filling and maintaining solder in baths and pots.

Dip soldering may be very useful and economical inasmuch as an entire unit, comprising any number of joints, can be soldered merely by dipping the part in a bath of molten solder. The soldering of printed circuit boards is an excellent example. Most commonly a printed circuit is a sheet of insulating material carrying a pattern in copper foil. The pattern is the electrical connection between circuit components soldered to the board. These components can all be soldered simultaneously by dipping for 4 to 8 seconds. The temperature of the dipping bath should be between 475 and 525 F. Solder pots or solder baths permit work pieces to be dipped by hand or to be done mechanically.

A good example of mechanical operations is the soldering of

cans. Side seams of cans are soldered on a machine consisting of a solder-coated roll operating in a bath of molten solder. The roll revolves bringing molten solder up to the seam of the can, which moves rapidly along a roll parallel to the axis of the solder roll. A buffing wheel then removes excess solder from the cans.

Flame soldering is mostly a manual operation employing a torch and is widely used in plumbing, automotive body work, and for structural joints. However, flame heating is not restricted to manual operations. There are numerous automatic applications where the work is passed through a stationary flame.

Oven heating is another well-established industrial tool for soldering. A smooth conveyor arrangement passing through furnace ovens seems preferable. Since there is no practical way to add flux and/or solder during the trip through the furnace, the parts are stacked and fluxed with a preform of soldering alloy in place. As the parts pass into the furnace the entire assembly is heated to soldering temperature. Following this, the parts remain on the conveyor traveling for a sufficient length of time to reach the solidus temperature

of the particular solder alloy employed. This cooling period is important since there must be no movement between the members in order to achieve a quality joint.

There are numerous procedures used in industrial soldering, but regardless of the application the temperature of the solder is relatively low and lead emissions due to melting are not a serious air pollution problem. There are, however, other operations associated with the melting that may result in substantial emissions if not properly controlled. An example is the automatic side seam soldering of cans as reported by one establishment. After the soldering, the excess is wiped from the joint by a rotating cloth buffer which creates some dust. Hoods, exhaust ducts, and cyclone collectors are used, but there is some dust that escapes the system. Particles entering the system are in flake form, mostly about one-half inch diameter.

Particles exhausted to the atmosphere are in the order of 20 microns or smaller. When using solder averaging 40 percent lead, the emissions to the atmosphere as reported are 1.7 pounds of lead per ton of solder consumed. One large can manufacturing plant currently uses solder at the rate of



3,300 tons per year, and lead emissions are reported at an average of 15 pounds per day.

It has been reported that the lead in the solder consumed in the United States during 1970 was 69,707 tons <sup>1</sup>/<sub>—</sub>; however, there is a lack of information concerning the quantity used for can manufacture and various other purposes. Consequently, the estimates of lead emissions resulting from the manufacture and use of solder may vary considerably. For this report it has been assumed that lead emissions average 3 pounds per ton of lead contained in the solder and that emissions in the United States during 1970 totaled 110 tons.

The rationale for the above assumption is that emissions are more than 1.6 and less than 4.25 pounds per ton of lead contained in the solder. It has been reported that uncontrolled particulate emissions from pot furnaces at secondary lead smelters average 0.8 pound per ton processed <sup>2</sup>/<sub>—</sub>. In that case there is one melting operation, but when solder is

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

2- "Compilation of Air Pollutant Emission Factors (Revised)"; U. S. Environmental Protection Agency; Research Triangle Park, N. C.; Office of Air Programs; Publ. No. AP-42; Feb., 1972.

manufactured and used the metal is melted twice. The 4.25 pounds per ton of lead is based on the can manufacturing data. The 1.7 pounds per ton of solder is equivalent to 4.25 pounds per ton of lead.

## CABLE COVERING

Cables for communication over telephone and telegraph lines and underground cables for distributing electrical power are the two major types of electrical cables using lead coverings. Since the purpose of any cable sheathing is protection for wires and insulation from moisture and the corrosive attacks of soil and atmosphere, lead has been a popular covering material because it is chemically inert in the presence of many corrosive acids and salts occurring naturally. In addition, the plasticity and flexibility of lead permits coiling, easy handling during installation, and minimizes the threat of rupture.

In the lead press technique for cable sheathing, the following requirements prevail: (1) the lead must be pure, which discourages any use of re-melted or scrap lead; (2) oxidation is to be prevented during refilling and extrusion processes; and, (3) a uniform, concentric sheath must be produced. The three main types of presses used to meet these requirements are the vertical hydraulic press, the straight-through press, and the continuous extrusion press.

In the typical vertical press the lead tube is formed by

forcing lead at a temperature just below 600 F into a chamber surrounding the cable. The lead divides into two streams, surrounds the point holder, and welds together on the underside. The mass of lead then flows to the die and emerges as a lead tube. It is then spray cooled, passed through a water trough, smeared with a thin layer of tallow, and wound on a cable drum. The lead presses deliver 600 to 3,000 tons pressure and take 300 pounds to one ton of lead per charge. Lead is melted in a lead pot adjacent to the press so that molten lead can be run into the container by means of a trough. This is often accomplished in a reducing atmosphere to minimize or prevent oxidation.

The straight-through press produces a sheath free from a longitudinal seam. The press is set on a foundation inclined downwards about 10 degrees from the horizontal. The lead flows longitudinally and then radially inward toward the die. The container may hold a lead charge of 1,000 pounds and the complete cycle in the press takes between 11 and 13 minutes.

The continuous extrusion press differs from the two presses just described in one basic way. Vertical and straight-

through presses are operated intermittently. When the lead container is empty, the press is stopped to refill the container in preparation for the next sheathing operation. However, in the continuous press insulated cable travels through a stationary tube surrounded by a revolving steel cylinder equipped with screw threads which in turn is surrounded by a stationary barrel. In the press, molten lead is fed into one end where it solidifies as it passes through the screw feed and emerges as a seamless tube around the cable. In this press lead is not exposed to oxidation during container refilling, there is no seam, and temperature can be controlled to produce an exact, uniform product. Continuous production is usually more desirable and economically feasible.

Based on the information obtained from two cable covering plants using cyclone collectors and bag filters, lead emissions to the atmosphere ranged from 1.5 to 5.5 pounds per ton of lead processed and averaged 2.0 pounds per ton. Emissions were lead oxides and silicates. The particle size ranged from 0.015 to 5 microns.

Based on the information regarding the two plants, lead emissions to the atmosphere due to cable covering operations during 1970 totaled 50 tons.

## TYPE METAL

Type metal alloys contain lead, antimony, and tin. Each of these three elements is used to impart certain specific characteristics. Lead is the base ingredient because it is plentiful, relatively cheap, and alloys well with the other elements. Antimony makes the alloy harder and more wear-resistant, lowers the melting point, and provides for some expansion as the alloy passes from a liquid to a solid state. This last characteristic causes the metal to be forced into all the cracks, crevices, and corners of the letter or design engraved into the mold. Tin is added for toughness, delay of setting time, a smooth finish, and increased fluidity of the alloy at all temperatures.

At one time it was considered imperative that all type metals be made from new or "virgin" metals; however, this concept has changed. Today the preparation of type metal begins with secondary lead from many sources including discarded batteries, lead pipe, scrap-type metals, and drosses. As necessary, the scrap materials are processed in reverberatory, blast, and/or pot furnaces. Then the product is brought up to specification by further metal additions prior to casting

in the form of bars, ingots, pigs, or feeders.

The chemical composition of a type-metal alloy determines its elementary or basic value, but to obtain satisfactory casting results the components must be homogeneously mixed to form the perfect alloy. The alloy having the lowest melting point is approximately 4 percent tin, 11.5 percent antimony, and 84.5 percent lead. That is the formula for linotype metal. All other type-metal alloys contain more tin and more antimony, thus increasing the alloy's melting point.

Type metals are classified into four principal groups. Linotype alloys are used in machines casting type metal by the line. The linotype metal must be of correct composition or it could freeze in the portholes of the casting machine, since operations are usually carried out at about 525 to 560 F.

Sterotype metal contains more tin and antimony and less lead than linotype. The stereotype process produces a number of like articles from the same mold known as a mat. The mat is made from some other source such as a form of linotype metal or a zinc engraving plate. It is one of the most sensitive of the type metals and represents a very large part of all type-metal alloys used. Sterotyping differs from other

typecasting processes mainly in: (1) size of the casting; (2) flow of metal; and, (3) use of a nonmetallic surface against which the metal is molded. Monotype alloys are used where each single character is cast on a piece of metal. Again there are increased amounts of tin and antimony. Electrotpe alloys are used for backing up "shells" of copper or nickel which do the actual printing. These alloys all contain less antimony and tin with increased amounts of lead varying from 90 to 96 percent.

In a printing plant, such as a metropolitan newspaper, large quantities of type metal are melted and remelted. The alloy is used again and again from day to day, and it is also circulated between the printer and the supplier. When a day's printing is complete much of the metal used may be remelted for type casting again the next day. Some cleaning is required and this can be accomplished by the printer. After a certain amount of reuse, however, the type metal is returned to the supplier for refining.

During this study a limited amount of information was obtained regarding lead emissions due to the use of type metal. Data was requested from nine large metropolitan newspapers,



but only three answered with one furnishing emission data. The one plant, during 1970, remelted 37,000 tons of type metal and purchased 104 tons to make up for losses. Tests were conducted during April, 1971, and spectrographic analyses showed that particulate emissions averaged 62 percent non-combustible materials and 40 percent lead. Total lead emissions were calculated to be 3.9 pounds per day, or 1,425 pounds per year.

The quantity of lead used in type metal during 1970 has been reported to be 24,476 tons <sup>1</sup>/<sub>1</sub>, and the data from the one newspaper indicates lead emissions are about 17 pounds per ton of lead contained in the alloy. On this basis, lead emissions in the United States during the year totaled about 200 tons.

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

## BRASS AND BRONZE

Lead is an alloying element in many brasses and bronzes.

In the various classifications of red and yellow brass, it is found in quantities ranging from less than one to more than 7 percent. In the high leaded bronzes, however, there may be as much as 25 percent lead.

During the processing of brass and bronze the metals may be melted together in a crucible, rotary, or reverberatory furnace which may vary in size from several hundred to several thousand pounds in capacity. The metal is poured and cast at temperatures ranging from 1,200 to 2,400 F, the actual temperature depending upon the alloy. The molds used to form slabs, cakes, and billets are cast iron, water-cooled, and often copper-lined. After casting the shapes may be rolled into plate, sheet, and strip; extruded into rods, bars, and seamless tubes; or drawn into wire. Final finishing operations include flattening, straightening, slitting, and cutting.

The emissions of lead and other pollutants vary in composition and concentration with the type of furnace, the alloy, and the foundry practice as indicated by the data in Table IV.

TABLE IV  
BRASS-MELTING FURNACE  
AND BAGHOUSE COLLECTOR DATA

Case	A	B	C
<u>Furnace Data</u>			
Type of furnace	Crucible	Crucible	Low-frequency induction
Fuel used	Gas	Gas	Electric
Metal melted	Yellow brass	Red brass	Red brass
Composition of metal melted, %			
Copper	70.6	85.9	82.9
Zinc	24.8	3.8	3.5
Tin	0.5	4.6	4.6
Lead	3.3	4.4	8.4
Other	0.8	1.3	0.6
Melting rate, lb/hr	388	343	1,600
Pouring temperature, F	2,160	2,350	2,300
Slag cover thickness, in.	1/2	1/2	3/4
Slag cover material	Glass	Glass	Charcoal
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<u>Baghouse Collector Data</u>			
Volume of gases, cfm	9,500	9,700	1,140
Type of baghouse	Sectional tubular	Sectional tubular	Sectional tubular
Filter material	Orlon	Orlon	Orlon
Filter area, ft <sup>2</sup>	3,836	3,836	400
Filter velocity, fpm	2.47	2.53	2.85
Inlet fume emission rate, lb/hr	2.55	1.08	2.2*
Outlet fume emission rate, lb/hr	0.16	0.04	0.086
Collection efficiency, %	93.7	96.2	96.0

\*Includes pouring and charging operations.

Data obtained from companies processing approximately 10 percent of the brass and bronze produced during 1970 indicates that lead emissions average about 4 pounds per ton of lead contained in the product. Since the lead used in brass and bronze totaled 18,927 tons during the year 1/, lead emissions to the atmosphere in the United States have been estimated at 40 tons.

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

## BEARING METALS

The most common bearing metals containing lead include copper-lead alloys, bronzes, and various babbitts which are prepared in a manner similar to other alloys. Primary lead may be melted in desired amounts with other metals, or "secondary metals" may be refined and adjusted to specification.

The lead and tin alloys invented by Issac Babbitt are based on the lead-antimony-tin system containing 9 to 16 percent antimony and up to 12 percent tin. The remainder is lead, with very small amounts of copper and arsenic. The lower cost of these alloys has been a primary factor in their popularity and they have been used extensively in automotive and diesel engines, outboard motors, lawn mowers, compressors, and earth-moving equipment.

Even in situations where stronger materials are needed for the actual bearings, babbitts are often employed as a thin surface coating. For large bearings in electric motors, turbines, blowers, and industrial equipment, finished babbitt may be 1/16 to 3/8 inch thick. Careful attention must be given to the details of each step in cleaning the bearing shell,

rinsing, fluxing, tinning, and casting to secure a sound bond. For smaller bearings and bushings used in fractional horsepower motors, a bimetal strip is produced by casting babbitt onto steel. The strip is then cut to size and the pieces formed into finished bearings. Where bearings require very high fatigue strength, three-layer strip bearings find use. They consist of a low carbon steel backing, an intermediate layer of metal, and a thin overlay of lead babbitt added by electroplating or precision casting.

Bronzes are used often for cast bushings since they combine economy with adequate bearing properties as well as good casting and machining characteristics. Leaded bronzes are usually used for intermediate load applications such as electric motors, outboard motors, farm equipment, and railroad cars. Tin bronzes are found in various heavy-duty applications. The very high strength bronzes appear in power shovels and heavy earth-moving equipment as they display excellent wear and impact resistance.

Copper-lead alloy bearings are used principally in engines where high fatigue strength and high temperature performance are required. Both main and connecting-rod bearings

in internal combustion engines for aircraft, automobiles, trucks, and diesels use these alloys, but they are also found in steam engines, electric motors, and turbines. These bearings are often made with a steel backing and a thin bab-bitt overlay. Premixed powders of 65 to 76 percent copper and 35 to 44 percent lead are usually the starting materials. The powder is spread on a continuously moving steel strip, sintered, rolled, resintered to improve the bond, and then rolled to size and formed into bearings.

The information obtained from industry during this study indicates that lead emissions resulting from bearing manufacture are negligible, even though air pollution control equipment is rarely used in connection with melting and alloying operations.

## METALLIC LEAD PRODUCTS

During the year 1970 approximately 122,000 tons of lead were used in the United States for terne metal, weights and ballasts, caulking lead, plumbing supplies, roofing materials, casting metal, foil, collapsible tubes, sheet lead, galvanizing, annealing, and lead plating <sup>1</sup>/. In most instances the lead was processed for these uses by melting and casting, followed by mechanical forming operations such as extruding or rolling. Sometimes it was necessary to melt the metal more than once.

From the standpoint of lead emissions to the atmosphere, it was determined during this study that most companies producing metallic lead products do not use air pollution control equipment unless it is required in connection with their other manufacturing operations. Reports from these companies indicate that their atmospheric emissions range from less than 0.5 to 4.3 pounds per ton of lead processed. Based on this information, the Contractor's estimate is that lead emissions resulting from the manufacture of metallic lead products

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.



average 1.5 pounds per ton of lead processed and emissions in the United States during 1970 totaled 90 tons.

## MISCELLANEOUS

There were several uses of lead during 1970, which totaled about 15,000 tons, that have not been discussed elsewhere in this report. They include ceramics, glass, plastics, fusible alloys, powdered lead greases, pesticides, and several other lesser applications.

In the ceramics industry lead is used mostly in the form of oxides and silicates in the manufacture of certain glasses, glazes, and vitreous enamels. Glass high in lead has a higher index of refraction, greater density, lower thermal conductivity, and greater chemical stability than unleaded glass. These characteristics impart greater brilliance, resonance, and toughness to the product. Lead also imparts its radiation absorption quality in proportion to the quantity contained in the glass. Optical glass, the finest glass tableware, most glass for electrical purposes, and windows for radiation shielding all contain large amounts of lead.

Lead is an important part of the composition of some fusible alloys, such as those used in sprinkler heads for spraying water at predetermined temperatures and those used in foundries to protect molds. It is also used as a vibration

dampener. Lead-asbestos pads have been used for this purpose under building and machinery foundations.

A growing use of lead compounds is in stabilizers for plastics. Polyvinyl chloride is a material which softens when heated and may be shaped into a variety of useful products. Unfortunately, however, it not only softens but also begins to degrade chemically. The stabilizers slow down this process so that the material is practical for usage.

In pesticides, lead arsenate is the only lead compound of commercial importance. Litharge is reacted with arsenic acid in the presence of an acetic acid catalyst to produce lead arsenate. The batches of several thousand gallons are heated to about 160 F and agitated for approximately 2 hours. The resulting lead arsenate precipitate is subsequently pumped to a drier from which the dry powder is conveyed to storage or the shipping department. Lead arsenate is sometimes used in dry powder form and sometimes applied in solution.

Quantitative data are lacking regarding lead emissions to the atmosphere due to the manufacture and miscellaneous uses of lead.

## OTHER SOURCES OF LEAD EMISSIONS

### WASTE OIL

It has been estimated that about 70 percent of the lead used in gasoline additives is discharged from the engine directly into the atmosphere, while the other 30 percent remains in the engine and exhaust system as deposits or becomes a contaminant in the lubricating oil.

One report indicates that the quantity of waste lubricating oil generated each year is currently in the order of 625 million gallons, and that about 55 percent is either dumped or used as road oil <sup>1</sup>/<sub>2</sub>. Most of the remaining 281 million gallons is re-refined as lubricating oil or reprocessed to fuel oil. It has been estimated that re-refining currently consumes 100 to 125 million gallons <sup>2</sup>/<sub>3</sub>; therefore, the amount used as fuel oil is approximately 160 million gallons annually.

Since waste crankcase oil contains about one percent lead by

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1- "Manual for Disposal of Liquid Petroleum Wastes"; Sun Oil Company; Philadelphia, Pa.; 1968.

2- Schmidt, P. F.; "Fuel Oil Manual"; 3rd Ed.; Industrial Press, Inc.; New York, N. Y.; 1969.

weight 1/, the quantity used as fuel oil during 1970 contained about 6,400 tons of lead. Assuming that 50 percent of the lead is discharged to the atmosphere during combustion, the lead emissions during the year were in the order of 3,200 tons.

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1- Final Report of the API Task Force on Used Oil Disposal; API Committee for Air and Water Conservation; American Petroleum Institute; New York, N. Y.; 1970.

## MUNICIPAL INCINERATION

Incineration is a combustion process and can be a source of considerable air pollution unless carefully controlled. Often poor design, management, and operator judgement are responsible for excessive emissions.

The sources of lead emissions during refuse incineration are refuse dumping and handling, smoke emissions around openings and through cracks in furnace walls, and the particulate discharged from the stack. The magnitude of the emissions is dependent principally upon the equipment design, the refuse composition, and the operating procedures. If the furnace is designed so that complete combustion can be achieved without undue difficulty, then it must be operated within the design parameters. The refuse charging rate must be maintained within the design range, the combustion air must be sufficient for complete combustion, and the condition of the refuse must be controlled within satisfactory limits. Even though the incinerator equipment is properly designed and operated, the emission rates will vary with the ash content of the refuse and the efficiency of the dust collecting system.

Of the 190 million tons of solid wastes collected in 1967, 8 percent (about 15 million tons) was burned in municipal incinerators 1/. It is estimated that the quantity burned in 1970 was 20 million tons. Tests at 2 municipal incinerator locations indicate that uncontrolled lead emissions are 0.42 pound per ton of charge, and lead emissions controlled by electrostatic precipitators average 0.06 pound per ton 2/. Calculations based on 50 percent control reveal that lead emissions to the atmosphere due to municipal incineration during 1970 totaled 2,400 tons.

$$\frac{0.42 \times 10^7}{2,000} + \frac{0.06 \times 10^7}{2,000} = 2,400$$

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1- "Control Techniques for Particulate Air Pollutants"; NAPCA; Public Health Service Publ. No. AP-51; Jan., 1969.

2- Source Test Nos. 71-CI-05 and 71-CI-11.

## SEWAGE AND SLUDGE INCINERATION

A recent report, released for publication during 1972, contains considerable information concerning the incineration of sewage sludge at South Lake Tahoe, California; Barstow, California; and Fairfax County, Lorton, Virginia. The sludge, particulate, stack gas, scrubbing liquid, and ash were sampled and analyzed for lead and other heavy metals. This data is included in the report along with a description of the incinerator equipment <sup>1</sup>/<sub>1</sub>.

Information from the report is shown as follows:

South Lake Tahoe, California	Multiple hearth incinerator. Design capacity - 900 lbs. per hour dry solids. Control device - Single cross flow perforated plate scrubber (6" H <sub>2</sub> O pressure drop). Test feed rate - 271 lbs. per hour average. Particulate emissions - 0.423 lbs. per hour (total) average. Lead in particulate - 1.4 percent average.
Barstow, California	Fluidized bed reactor. Design capacity - 500 lbs. per hour dry solids.

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1- "Sewage and Sludge Incineration"; EPA Task Force;  
Program Element B12043; Mar., 1972.



Control device - Single cross-flow perforated plate scrubber (4" H<sub>2</sub>O pressure drop).

Test feed rate - 462 lbs. per hour average.

Particulate emissions - 0.742 lbs. per hour (total) average.

Lead in particulate - 0.08 percent average.

Fairfax County,  
Lorton, Virginia

Multiple hearth incinerator.

Design capacity - 2,500 lbs. per hour dry solids.

Control device - Cyclone inertial jet scrubber (2.5" H<sub>2</sub>O pressure drop).

Test feed rate - 1,223 lbs. per hour average.

Particulate emissions - 0.198 lbs. per hour (total) average.

Lead in particulate - 0.9 percent average.

Based on the above data, calculations indicate that lead emissions from the 3 incinerators varied from about 0.0026 to 0.044 pound per ton of charge, averaging 0.025 pound per ton. Assuming that the efficiency of the scrubbers was 97 percent, the emission factor was 0.6 pound per ton (uncontrolled).

It is estimated that the sludge burning rate in the United States during 1970 was about 2,000 tons per day <sup>1</sup>/<sub>1</sub>. Accordingly, the lead emissions due to the burning of sludge are estimated on the basis of 10 percent control at approximately 200 tons for 1970.

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1- Private communication with the Federal Water Pollution Control Authority.

## COAL

In order to estimate lead emissions to the atmosphere due to the use of coal, information was obtained regarding the quantity of coal produced in various states, its lead content, the quantity consumed during 1970, and the efficiency of dust collecting equipment in use at coal-burning plants.

The Bureau of Mines, the Geological Survey, and others have conducted numerous studies to determine the trace element content of various coals; it has been found that lead concentrations vary considerably from region to region. One report covering the analyses of 827 samples of commercial coals <sup>1/</sup> indicates that those from areas near the Missouri lead belt contain considerably more lead than those from other parts of the country. Coal from Illinois, Iowa, and Missouri averages 31 to 33 ppm lead, while that from other states averages from 0.6 to 10.5 ppm. As shown in Table V this difference is significant. The Illinois coal accounts for nearly 43 percent of the lead in the coal produced during 1970.

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1- Abernethy, R. F., Peterson, M. J., and Gibson, F. H.; "Spectrochemical Analyses of Coal Ash for Trace Elements"; Bureau of Mines RI 7281; July, 1969.

TABLE V  
LEAD CONTENT OF COAL  
MINED IN THE UNITED STATES

State	Average Ash of Dry Coal <sup>1/</sup>	Average Pb % in Coal Ash <sup>1/</sup>	Average Pb Content of Coal - ppm	1970 Coal Production 1000 Tons <sup>2/</sup>	Pb in Coal Tons
Alabama	9.2	0.0040	3.7	20,560	76
Alaska			7.0*	549	4
Arizona	9.7	0.0040	3.9	132	1
Arkansas	8.3	0.0035	2.9	268	1
Colorado	9.2	0.0031	2.9	6,025	17
Illinois	11.7	0.0279	32.6	65,119	2,120
Indiana	10.6	0.0068	7.2	22,263	155
Iowa	15.5	0.0200	31.0	987	31
Kansas	10.5	0.0100	10.5	1,627	17
Eastern Kentucky	7.3	0.059	4.3	72,502	312
Western Kentucky	9.3	0.0069	6.4	52,803	338
Maryland	9.5	0.0010	1.0	1,615	2
Missouri	12.4	0.0267	33.1	4,447	147
Montana	12.6	0.0038	4.8	3,447	17
New Mexico	11.8	0.0040	4.7	7,361	35
North Dakota	12.0	0.0022	2.6	5,639	15
Ohio	11.8	0.0043	5.1	55,351	282
Oklahoma			7.0*	2,427	17
Pennsylvania	10.0	0.0052	5.2	80,491	418
Tennessee	9.7	0.0050	4.9	8,237	40
Utah	7.0	0.0024	1.7	4,733	8
Virginia	7.8	0.0078	6.1	35,016	214
Washington	12.7	0.0025	3.2	37	-
West Virginia	8.5	0.0058	4.9	144,072	705
Wyoming	8.7	0.0007	0.6	7,222	4
TOTAL				602,930	4,976
*Estimated					

1- Abernethy, R. F., Peterson, M. J., and Gibson, F. H.; "Spectrochemical Analyses of Coal Ash for Trace Elements"; Bureau of Mines RI 7281; July, 1969.

2- "Advance Data on Coal - Bituminous and Lignite in 1970"; Mineral Industry Surveys; Bureau of Mines; Feb. 7, 1972.

Lead emissions to the atmosphere resulting from the use of coal are primarily those that occur in connection with the production of steam. During 1970 the electric utility companies burned about 62 percent of the bituminous coal and lignite to make steam for driving turbo-generators that produce electric energy. The remaining 38 percent was used mostly by manufacturing and mining companies to make steam for various heating and processing operations <sup>1</sup>/<sub>.</sub>

Currently most of the steam generated by burning coal is produced in relatively large combustion units that are equipped with a dust collecting system. Electrostatic precipitators and mechanical cyclone collectors are the types of equipment used in nearly every plant. As the coal is burned, a considerable portion of the ash is carried upward with the flue gas through the boiler to the dust collection system, where most of the ash is removed before the flue gas is discharged to the atmosphere.

Information obtained from the Federal Power Commission in the form of a computer print-out shows the design efficiency

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1- "Advance Data on Coal - Bituminous and Lignite in 1970"; Bureau of Mines; Mineral Industry Surveys; Feb. 7, 1972.

of dust collectors and the quantity of coal consumed at electric utility plants in the United States. Using that information, average overall dust collection efficiencies have been estimated and calculations have been made based on:

- (a) 602,930,000 tons of bituminous coal and lignite produced during 1970, containing 4,976 tons of lead (see Table V);
- (b) 517,158,000 tons of bituminous coal and lignite consumed during 1970 <sup>1</sup>/<sub>1</sub>, containing 4,270 tons of lead (based on Table V);
- (c) fly ash 65 percent of total ash;
- (d) 85 percent average overall dust collection efficiency;
- (e) 90 percent application of control.

The lead emissions calculated in this manner totaled 650 tons during 1970.

$$4,270 \times 0.65 \left[ 1 - (0.85 \times 0.90) \right] = 650$$

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1- "Advance Data on Coal - Bituminous and Lignite in 1970";  
Bureau of Mines; Mineral Industry Surveys; Feb. 7, 1972.

## OIL

While this study was in progress several large oil refining companies were contacted for the purpose of obtaining reliable data regarding the lead contained in the various foreign and domestic fuel oils used in the United States. Unfortunately, nothing was available concerning the oil used in 1970; however, some useful information was obtained from one company concerning the oil refined in 1967.

During refining, the metallic elements (including lead) found in crude oil concentrate in the residual fuel. Data compiled in 1967 show that residual oil (No. 6 fuel oil) produced from domestic crude averaged 20 ppm of lead, while that produced from foreign crude averaged  $0.8 \text{ ppm } \frac{1}{\text{.}}$ . This data represents the average of numerous tests of products of one oil refining company rather than industry averages, and does not include low-sulfur residuals from Libyan or Nigerian crudes.

The residual oil consumed in the United States during 1970

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1- Private communication.

was 804 million barrels <sup>1</sup>/<sub>1</sub>. Approximately 72 percent (580 million barrels) was produced from foreign crude oils and 28 percent (224 million barrels) from domestic crudes.

Based upon the above lead concentrations and an average weight of 340 pounds per barrel, the residual oil from foreign crudes contained about 80 tons of lead and that from domestic crudes about 760 tons.

Substantially different results were obtained, however, when using data from another source. Out of 101 samples of domestic crude, 92 samples contained from 0.0003 to 11.4 ppm of lead and 9 samples contained no lead. The average for the 101 samples was 0.29 ppm of lead <sup>2</sup>/<sub>1</sub>. The domestic production of crude oil during 1970 was 3,350 million barrels <sup>3</sup>/<sub>1</sub>. Calculations using these figures indicate that domestic crude contained 165 tons of lead.

A third source of information gives emission factors in

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

2- Horr, C. A. et al; "Uranium and Various Other Metals in Crude Oils"; Geological Survey Bulletin 1100; 1961.

3- Mineral Industry Surveys; "Sales of Fuel Oil and Kerosine in 1970"; Oct. 1, 1971.

terms of pounds of lead per million gallons of fuel oil for distillate oil fired in residential units and for residual oil fired in commercial boilers. An average of 3 tests burning distillate oil indicates that lead emissions are about 3 pounds per million gallons of fuel (0.1 pound per 1,000 bbls), and 3 tests burning residual oil show 1.5 pounds of lead per million gallons (0.06 pound per 1,000 bbls)  $\frac{1}{2}$ . Based on these emission factors, the 927 million barrels of distillate oil used in 1970  $\frac{2}{2}$  resulted in lead emissions totaling about 65 tons, and the 804 million barrels of residual oil accounted for lead emissions of 25 tons.

The total lead emissions due to the use of fuel oil in the United States during 1970 are estimated by the Contractor at 90 tons.

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1- Levy, A., Miller, S. E., Barrett, R. E., Schulz, E. J., Melvin, R. H., Axtman, W. H., and Locklin, D. W.; "A Field Investigation of Emissions from Fuel Oil Combustion for Space Heating"; Battelle - Columbus; Presented at American Petroleum Institute Committee on Air and Water Conservation Meeting at Columbus, Ohio; Nov. 1, 1971.

2- Mineral Industry Surveys; "Sales of Fuel Oil and Kerosine in 1970"; Oct. 1, 1971.



## IRON AND STEEL

There are numerous documents that contain information related to lead emissions to the atmosphere from steel mills. It is thought that most of the emissions occur due to the use of iron ore that contains trace amounts of lead, the use of lead-bearing scrap, the production of ferromanganese, and the manufacture of leaded steel alloy. There are direct references concerning the analyses of particulate samples collected at the discharge of open-hearth, electric, and basic oxygen furnaces. Also, there is information showing the quantity of particulate emitted from various steelmaking operations.

It is estimated that dusts containing more than 10,000 tons of lead are produced by the steelmaking industry each year. A Bureau of Mines report states that 340 dust samples from 48 operators were analyzed for metal content. The lead contained in the dust from open-hearth, electric, and basic oxygen furnaces averaged 0.8, 2.0, and 0.4 percent, respectively <sup>1</sup>/<sub>.</sub>

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1- Barnard, P. G. et al; "Recycling of Steelmaking Dusts"; Bureau of Mines Solid Waste Program; Technical Progress Report - 52; Feb., 1972.

It was also noted that electric furnace dusts have a wider range composition due to the variation in lead content of the 100 percent scrap heats. The analyses of dusts from 18 electric furnaces showed that the contained lead varied from 0.17 to 5.7 percent.

Emission factors have been determined for particulate discharged from steelmaking operations <sup>1</sup>/<sub>—</sub> and are shown as follows:

Blast Furnace	-	160 lbs/ton (uncontrolled)
Open-Hearth	-	17 lbs/ton (uncontrolled)
Basic Oxygen	-	46 lbs/ton (uncontrolled)
Electric Arc	-	9 lbs/ton (uncontrolled)
Sintering	-	42 lbs/ton (uncontrolled)
Scarfig	-	20 lbs/ton (uncontrolled)

Based on the above data, emission factors for lead are:

Open-Hearth	-	0.14 lbs/ton (uncontrolled)
Basic Oxygen	-	0.18 lbs/ton (uncontrolled)
Electric Arc	-	0.18 lbs/ton (uncontrolled)

During 1970 the open-hearth steel production was 48 million tons <sup>2</sup>/<sub>—</sub>. Based on the above emission factor and 70 percent

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1- "Compilation of Air Pollutant Emission Factors (Revised)"; U. S. Environmental Protection Agency; Research Triangle Park, N. C.; Office of Air Programs; Publ. No. AP-42; Feb., 1972.

2- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

control, the lead emissions were about 1,000 tons.

Basic oxygen steel production was 63.3 million tons during 1970 <sup>1</sup>/<sub>1</sub>. At 99 percent control, the lead emissions were nearly 60 tons during the year.

Electric arc steel production for 1970 was 20.2 million tons <sup>1</sup>/<sub>1</sub>. Based on an emission factor of 0.18 lbs/ton and 78 percent control, the lead emissions during the year totaled 400 tons.

Due to lack of data regarding the lead content of dust from blast furnace, sintering, and scarfing operations, the lead emissions from these sources have not been estimated. It does seem likely, however, that the total for these might be as much as the total from the open-hearth, electric, and basic oxygen furnaces.

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

## GREY IRON FOUNDRIES

During this study spectrographic analyses of dust samples from three iron foundries were examined. Lead was contained in each sample, the amount ranging from 0.5 to 2.0 percent, and averaging 1.2 percent <sup>1</sup>/<sub>1</sub>.

The cupola is the most popular method for producing cast iron. The rate of particulate emissions from this type of furnace has been reported as 4 to 26 pounds per ton of process weight not including emissions from materials handling, charging, or other non-melting operations. A cupola emission factor of 17 pounds per ton of metal charged (uncontrolled) has been determined <sup>2</sup>/<sub>2</sub>.

Based on the information obtained from industry, the particulate emission factor is estimated at 22 pounds per ton of process weight, including melting and non-melting operations. The degree of emission control is estimated at 25 percent. Calculations show that with 1.2 percent lead in the particulate,

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1- Private communication.

2- "Compilation of Air Pollutant Emission Factors (Revised)": U. S. Environmental Protection Agency; Research Triangle Park, N. C.; Office of Air Programs; Publ. No. AP-42; Feb., 1972.

the emission factor is 0.26 pound of lead per ton of process weight (uncontrolled).

During 1970 the production at grey iron foundries was reported as 24 million tons <sup>1</sup>/<sub>—</sub>; therefore, lead emissions to the atmosphere totaled 2,300 tons.

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1- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

## FERROALLOYS

During this study a search revealed that very little data is available regarding lead emissions resulting from ferro-alloy processing. Emission factors for particulate have been established and studies have been conducted covering the effectiveness, cost, and use of air pollution controls. The area where more information is needed concerns the quantity of lead in the particulate.

The effluent from a ferromanganese blast furnace is reported to be a greater air pollution problem than that from an iron blast furnace <sup>1</sup>/<sub>1</sub>. It is said to be the most prolific pollution producer of any of the metallurgical processes <sup>2</sup>/<sub>2</sub>. A particulate emission factor of 410 pounds per ton (uncontrolled) has been established for the ferromanganese blast furnace operations, while the emission factor for electric furnaces is 45 pounds per ton <sup>3</sup>/<sub>3</sub>. For silicomanganese production in

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- 1- Thring, N. W. and Sarjant, R. J.; "Dust Problems of the Iron and Steel Industry"; Iron and Coal Traders Rev.; 174; Mar. 29, 1957.
  - 2- Wurts, T. C.; "Industrial Sources of Air Pollution - Metallurgical"; Public Health Service Publ. No. 654; 1959.
  - 3- "Compilation of Air Pollutant Emission Factors (Revised)"; U. S. Environmental Protection Agency; Research Triangle Park, N. C.; Office of Air Programs; Publ. No. AP-42; Feb., 1972.

electric furnaces the emission factor is 195 pounds per ton <sup>1</sup>/.

Information obtained from industry indicates that typical emissions from silicomanganese furnaces contain about 0.45 percent lead, while those from ferromanganese furnaces contain 0.90 percent <sup>2</sup>/.

During 1970 the production of silicomanganese and ferromanganese <sup>3</sup>/ was as follows:

Silicomanganese	- 119,000 tons
Ferromanganese	
Blast Furnace	- 501,000 tons
Electric Furnace	- 334,000 tons

Based on the above information the lead emissions for 1970 are estimated as follows:

	<u>Lead Emissions</u>
Production of silicomanganese (50 percent control)	- 25 tons
Production of ferromanganese	
Electric Furnace (40 percent control)	- 40 tons
Blast Furnace (99 percent control)	- <u>10 tons</u>
	75 tons

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1- "Compilation of Air Pollutant Emission Factors (Revised)"; U. S. Environmental Protection Agency; Research Triangle Park, N. C.; Office of Air Programs; Publ. No. AP-42; Feb., 1972.

2- Private communication.

3- Minerals Yearbook; Bureau of Mines; 1970 Preprint.

## CEMENT PLANTS

There are four basic production steps in the manufacture of cement. They include quarrying, size reduction of the limestone rock, clinker production, and finish grinding. After quarrying, the rock is first crushed in primary and secondary crushers, then it goes through the grinding operation. Next, the raw materials are dried and calcined in a kiln to produce a cement clinker. Finally, the clinker is ground with gypsum and packaged for shipment.

Cement may be manufactured by the wet or dry process, but the principal difference is in the grinding step. In the wet process, water is introduced before grinding and the material is handled in a slurry until it reaches the kiln.

Although the kilns, dryers, and crushers are the major sources of particulate emissions, dust is produced in nearly every manufacturing step. Throughout processing the raw material is transported from point to point by conveyors. Even though hoods may be used over loading, unloading, and transfer points, the conveying equipment is a source of substantial emissions.



It has been determined that uncontrolled particulate emissions from the wet and dry processes are 44 and 64 pounds per barrel of cement, respectively  $\frac{1}{2}$ /. The average is, therefore, considered to be 54 pounds per barrel. The analyses of dust collected during source testing at four cement plants indicates that the lead content averages about 450 ppm  $\frac{2}{2}$ /. The cement produced during 1970 was 407 million barrels.

Based on the above data and an estimated 90 percent control, the lead emissions during 1970 totaled 500 tons.

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1- "Compilation of Air Pollutant Emission Factors (Revised)"; U. S. Environmental Protection Agency; Research Triangle Park, N. C.; Office of Air Programs; Publ. No. AP-42; Feb., 1972.

2- Source Test Nos. 71-MM-01, 71-MM-02, 71-MM-03, and 71-MM-05.

### UPDATING OF EMISSION ESTIMATES

Since the scope of work for this study specifically excluded field testing, the emission estimates presented are the results of calculations based on: (1) test data where available; (2) reports from industry; (3) direct observations; or, (4) a combination of published data and assumptions. It is believed that the most accurate estimates are those based on the test data and the industry reports; however, in most instances the number of tests are limited to two or three and their average may not always be representative of the average for the industry.

The estimates based on test data include those for:

- Municipal Incineration
- Sewage and Sludge Incineration
- Distillate Oil Combustion
- Residual Oil Combustion
- Iron and Steel Production
- Grey Iron Foundries
- Cement Plants

It is recommended that more source tests be conducted for all categories, except Iron and Steel Production.

The emission estimates based on industry reports include:

Primary Lead  
Secondary Lead  
Lead Oxide Production  
Storage Batteries  
Gasoline Additive Manufacture  
Pigments  
Cable Covering  
Type Metal  
Brass and Bronze

The estimates for primary and secondary lead, lead oxide production, storage batteries, and gasoline additive manufacture are believed to be reasonably accurate. They are based on information obtained from a large percentage of the producers and, therefore, it is doubtful that updated estimates would yield more accurate results. On the other hand, information obtained from manufacturers of pigments, cable covering, type metal, and brass and bronze was limited. Additional information in the form of source test data would unquestionably improve the accuracy of those estimates.

With respect to mining and milling, the emission factor shown in this report was determined by direct observation. Several plants were visited while milling was in progress. In addition, some information was obtained during conversations with the operating personnel. It is recommended that source tests be conducted.

For lead emissions resulting from primary copper and zinc smelting, solder manufacture, waste oil and coal combustion, and ferroalloy production, certain assumptions were made to supplement published information. Again, source testing is recommended as the method for improving the accuracy of emission estimates.

<b>BIBLIOGRAPHIC DATA SHEET</b>	1. Report No.	2.	3. Recipient's Accession No.
4. Title and Subtitle Emission Study of Industrial Sources of Lead Air Pollutants 1970		5. Report Date April 1973	6.
7. Author(s) W. E. Davis		8. Performing Organization Repr. No.	
9. Performing Organization Name and Address W. E. Davis 9726 Sagamore Road Leawood, Kansas		10. Project/Task/Work Unit No.	
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