12.16 Lead Oxide And Pigment Production

12.16.1 General[1-2,7]

Lead oxide is a general term and can be either lead monoxide or "litharge" (PbO); lead tetroxide or "red lead" (Pb_3O_4); or black or "gray" oxide which is a mixture of 70 percent lead monoxide and 30 percent metallic lead. Black lead is made for specific use in the manufacture of lead acid storage batteries. Because of the size of the lead acid battery industry, lead monoxide is the most important commercial compound of lead, based on volume. Total oxide production in 1989 was 57,984 megagrams (64,000 tons).

Litharge is used primarily in the manufacture of various ceramic products. Because of its electrical and electronic properties, litharge is also used in capacitors, Vidicon® tubes, and electrophotographic plates, as well as in ferromagnetic and ferroelectric materials. It is also used as an activator in rubber, a curing agent in elastomers, a sulfur removal agent in the production of thioles and in oil refining, and an oxidation catalyst in several organic chemical processes. It also has important markets in the production of many lead chemicals, dry colors, soaps (i. e., lead stearate), and driers for paint. Another important use of litharge is the production of lead salts, particularly those used as stabilizers for plastics, notably polyvinyl chloride materials.

The major lead pigment is red lead (Pb_3O_4), which is used principally in ferrous metal protective paints. Other lead pigments include white lead and lead chromates. There are several commercial varieties of white lead including leaded zinc oxide, basic carbonate white lead, basic sulfate white lead, and basic lead silicates. Of these, the most important is leaded zinc oxide, which is used almost entirely as white pigment for exterior oil-based paints.

12.16.2 Process Description[8]

Black oxide is usually produced by a Barton Pot process. Basic carbonate white lead production is based on the reaction of litharge with acetic acid or acetate ions. This product, when reacted with carbon dioxide, will form lead carbonate. White leads (other than carbonates) are made either by chemical, fuming, or mechanical blending processes. Red lead is produced by oxidizing litharge in a reverberatory furnace. Chromate pigments are generally manufactured by precipitation or calcination as in the following equation:

$$Pb(NO_3)_2 + Na_2(CrO_4) \rightarrow PbCrO_4 + 2\ NaNO_3 \qquad (1)$$

Commercial lead oxides can all be prepared by wet chemical methods. With the exception of lead dioxide, lead oxides are produced by thermal processes in which lead is directly oxidized with air. The processes may be classified according to the temperature of the reaction: (1) low temperature, below the melting point of lead; (2) moderate temperature, between the melting points of lead and lead monoxide; and (3) high temperature, above the melting point of lead monoxide.

12.16.2.1 Low Temperature Oxidation -

Low temperature oxidation of lead is accomplished by tumbling slugs of metallic lead in a ball mill equipped with an air flow. The air flow provides oxygen and is used as a coolant. If some form of cooling were not supplied, the heat generated by the oxidation of the lead plus the mechanical heat of the tumbling charge would raise the charge temperature above the melting point of lead. The ball mill product is a "leady" oxide with 20 to 50 percent free lead.

12.16.2.2 Moderate Temperature Oxidation -

Three processes are used commercially in the moderate temperature range: (1) refractory furnace, (2) rotary tube furnace, and (3) the Barton Pot process. In the refractory furnace process, a cast steel pan is equipped with a rotating vertical shaft and a horizontal crossarm mounted with plows. The plows move the charge continuously to expose fresh surfaces for oxidation. The charge is heated by a gas flame on its surface. Oxidation of the charge supplies much of the reactive heat as the reaction progresses. A variety of products can be manufactured from pig lead feed by varying the feed temperature, and time of furnacing. Yellow litharge (orthorhombic) can be made by cooking for several hours at 600 to 700°C (1112 to 1292°F) but may contain traces of red lead and/or free metallic lead.

In the rotary tube furnace process, molten lead is introduced into the upper end of a refractory-lined inclined rotating tube. An oxidizing flame in the lower end maintains the desired temperature of reaction. The tube is long enough so that the charge is completely oxidized when it emerges from the lower end. This type of furnace has been used commonly to produce lead monoxide (tetragonal type), but it is not unusual for the final product to contain traces of both free metallic and red lead.

The Barton Pot process (Figure 12.16-1) uses a cast iron pot with an upper and lower stirrer rotating at different speeds. Molten lead is fed through a port in the cover into the pot, where it is broken up into droplets by high-speed blades. Heat is supplied initially to develop an operating temperature from 370 to 480°C (698 to 896°F). The exothermic heat from the resulting oxidation of the droplets is usually sufficient to maintain the desired temperature. The oxidized product is swept out of the pot by an air stream.

The operation is controlled by adjusting the rate of molten lead feed, the speed of the stirrers, the temperature of the system, and the rate of air flow through the pot. The Barton Pot produces either litharge or leady litharge (litharge with 50 percent free lead). Since it operates at a higher temperature than a ball mill unit, the oxide portion will usually contain some orthorhombic litharge. It may also be operated to obtain almost entirely orthorhombic product.

12.16.2.3 High Temperature Oxidation -

High temperature oxidation is a fume-type process. A very fine particle, high-purity orthorhombic litharge is made by burning a fine stream of molten lead in a special blast-type burner. The flame temperature is around 1200°C (2192°F). The fume is swept out of the chamber by an air stream, cooled in a series of "goosenecks" and collected in a baghouse. The median particle diameter is from 0.50 to 1.0 micrometers, as compared with 3.0 to 16.0 micrometers for lead monoxide manufactured by other methods.

12.16.3 Emissions And Controls[3-4,6]

Emission factors for lead oxide and pigment production processes are given in Tables 12.16-1 and 12.16-2. The emission factors were assigned an E rating because of high variabilities in test run results and nonisokinetic sampling. Also, since storage battery production facilities produce lead oxide using the Barton Pot process, a comparison of the lead emission factors from both industries has been performed. The lead oxide emission factors from the battery plants were found to be considerably lower than the emission factors from the lead oxide and pigment industry. Since lead battery production plants are covered under federal regulations, one would expect lower emissions from these sources.

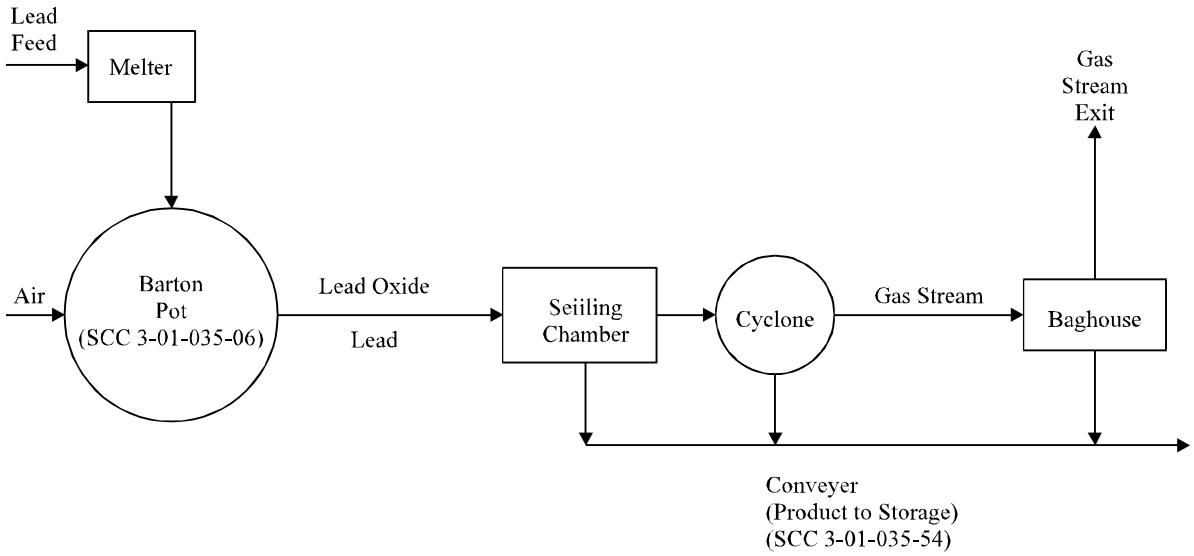

Figure 12.16-1. Lead oxide Barton Pot process.
(Source Classification Codes in parentheses.)

Automatic shaker-type fabric filters, often preceded by cyclone mechanical collectors or settling chambers, are the common choice for collecting lead oxides and pigments. Control efficiencies of 99 percent are achieved with these control device combinations. Where fabric filters are not appropriate, scrubbers may be used to achieve control efficiencies from 70 to 95 percent. The ball mill and Barton Pot processes of black oxide manufacturing recover the lead product by these 2 means. Collection of dust and fumes from the production of red lead is likewise an economic necessity, since particulate emissions, although small, are about 90 percent lead. Emissions data from the production of white lead pigments are not available, but they have been estimated because of health and safety regulations. The emissions from dryer exhaust scrubbers account for over 50 percent of the total lead emitted in lead chromate production.

Table 12.16-1 (Metric Units). CONTROLLED EMISSIONS FROM LEAD OXIDE AND PIGMENT PRODUCTION[a]

Process	Particulate		Lead		References
	Emissions	EMISSION FACTOR RATING	Emissions	EMISSION FACTOR RATING	
Lead Oxide Production					
Barton Pot[b] (SCC 3-01-035-06)	0.21 - 0.43	E	0.22	E	4,6
Calcining (SCC 3-01-035-07)					
Baghouse Inlet	7.13	E	7.00	E	6
Baghouse Outlet	0.032	E	0.024	E	6
Pigment Production					
Red lead[b] (SCC 3-01-035-10)	0.5[c]	B	0.50	B	4,5
White lead[b] (SCC 3-01-035-15)	ND	NA	0.28	B	4,5
Chrome pigments (SCC 3-01-035-20)	ND	NA	0.065	B	4,5

[a] Factors are for kg/Mg of product. SCC = Source Classification Code. ND = no data. NA = not applicable.
[b] Measured at baghouse outlet. Baghouse is considered process equipment.
[c] Only PbO and oxygen are used in red lead production, so particulate emissions are assumed to be about 90% lead.

Table 12.16-2 (English Units). CONTROLLED EMISSIONS FROM LEAD OXIDE AND PIGMENT PRODUCTION[a]

Process	Particulate		Lead		References
	Emissions	EMISSION FACTOR RATING	Emissions	EMISSION FACTOR RATING	
Lead Oxide Production					
Barton Pot[b] (SCC 3-01-035-06)	0.43 - 0.85	E	0.44	E	4,6
Calcining (SCC 3-01-035-07)					
Baghouse Inlet	14.27	E	14.00	E	6
Baghouse Outlet	0.064	E	0.05	E	6
Pigment Production					
Red lead[b] (SCC 3-01-035-10)	1.0[c]	B	0.90	B	4,5
White lead[b] (SCC 3-01-035-15)	ND	NA	0.55	B	4,5
Chrome pigments (SCC 3-01-035-20)	ND	NA	0.13	B	4,5

[a] Factors are for lb/ton of product. SCC = Source Classification Code. ND = no data. NA = not applicable.
[b] Measured at baghouse outlet. Baghouse is considered process equipment.
[c] Only PbO and oxygen are used in red lead production, so particulate emissions are assumed to be about 90% lead.

References For Section 12.16

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