

Pb

Lead

in the World of Ceramics

John S. Nordyke



The American Ceramic Society

Lead in the World of Ceramics

**A Source Book for Scientists,
Engineers, and Students**

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**Lead in the
World of Ceramics**

Dedication

For his lifelong devotion to excellence and for his unselfish leadership in the lead industry, this book is respectfully dedicated to William Peter Wilke III.

A Note of Appreciation

We express our appreciation for the work and cooperation of those authors who have contributed text material for this book. Aside from those chapters written by the Editor, eleven chapters have been written by contributing authors. Some of these chapters have been written by one person, others by as many as six. All were selected for their outstanding expertise in the subject covered. All have cooperated beautifully with us.

The following were selected as collaborators:

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Jerome F. Smith	Lead Industries Association, Inc

Their contributions are greatly appreciated.

A special note of appreciation is due to William R. Prindle, Corning Glass Works, for his valuable support of this book.

John S. Nordyke

Foreword

This book is intended to fill a need for a comprehensive review of the properties and uses of lead compounds in the area of ceramics. It is designed to provide engineers, chemists, and ceramists with the latest and most complete information on the use of lead compounds in all types of ceramic products and processes. The ultimate objective is the expanded use of lead chemicals in ceramics in an economically viable and environmentally acceptable manner.

An earlier manual, *Lead in the Ceramic Industries*, was published in 1956 by the Lead Industries Association as a convenient guide for the industrial ceramist. It provided typical formulas, firing procedures, and resulting properties. During the intervening quarter-century, many new applications of lead compounds were developed and commercialized in the ceramic industries. Additionally, ILZRO research contributed to the establishment of international standards for sampling, testing, and permissible limits of lead and cadmium release from ceramic foodware surfaces to assure the safety of the consuming public. These developments, along with results of other ILZRO research conducted over the past 2 decades, are incorporated in this volume.

Because of the diversity of applications for lead compounds in such products as ceramic glazes, glasses, enamels, colors, and electronic ceramics, and the need for plant safety and good occupational health practices, ILZRO called on John S. Nordyke, Vice President of Hammond Lead Products, Inc., to coordinate the preparation of chapters in each of these areas. On the basis of more than 50 years of experience, including the presidency of the American Ceramic Society, Mr. Nordyke was able to assemble a group of experts to write the required chapters in their own areas of expertise. Mr. Nordyke is eminently qualified for this task. Since graduating (with a B.S. in Chemistry) from the Oklahoma A & M College in 1931 (now Oklahoma State University), he worked with Eagle-Picher Lead Co. for 22 years in manufacturing, research, and sales. He has been with Hammond since 1953 in various capacities. During this time, he promoted research and development, which led to several new products, and collected 19 world patents along the way.

ILZRO also expresses its gratitude to the American Ceramic Society for assuming the task of publishing this volume.

Dr. S. F. Radtke
President
International Lead Zinc Research Organization, Inc.

Introduction

Lead may well have been the first metal to be smelted by early man. Beads of lead found at the site of Çatal Hüyük in present-day Turkey have been dated to about 6500 B.C.¹ (Neolithic). The alchemical symbol for lead, Pb , is the sign of Saturn, father of the gods. Much of the ancient mining and smelting of lead was carried out to recover silver, which is present in unrefined lead in varying amounts. The so-called silver mines at Laurion in Greece, were in reality, lead mines, with silver as the most desired product. This silver was the main source of the great wealth of Athens during the Age of Pericles, the Golden Age of Greece (fifth century B.C.). Recovery of lead, therefore, must have preceded that of silver. There is strong evidence that smelting of lead preceded that of copper by as much as 3000 years.²

In the recovery of silver from lead, the lead was burned at a temperature of about 1100°C, forming a slag of litharge (Greek: silver stone) and leaving unburned molten silver. In the earliest times, the market for litharge (lead monoxide) was small and the excess was cast aside in piles as waste. In later periods, these waste piles became rich sources for the recovery of lead metal.

Pottery is an ancient product, possibly much older than lead. Glass is also a venerable artifact and is one of man's earliest manufactured products. However, lead oxide and pottery did not come together in the form of glazed ware until sometime in the bronze age. Much unglazed pottery of the Neolithic age is displayed in the museums of China, the Middle East, and other areas of the world. William Pulsifer states: "Schliemann found at Mycenae objects resembling buttons which proved upon analysis to be composed of a strongly burned clay varnished with a lead glazing. . . It has also been stated that the glazing of pottery found in ancient Egyptian tombs is composed of lead, and there is also reason to believe that the glazing of bricks and other articles found at Nineveh and Babylon was produced in some cases by the use of litharge. Maigne states that the art was invented in the East and was supposed to have been known in the time of Solomon, and the research of modern archaeologists seems to confirm this suggestion. Eraclius, whose manuscript is attributed to the ninth or tenth century, describes the process minutely and gives directions for producing a variety of colors and tints in the glaze."² Thus, it is apparent that the lead and pottery industries have enjoyed a relationship of several thousands of years duration.

Schliemann² describes objects of lead glass found at "Sparta" (sic) in Greece (Sparta?) thought to date from the eighth century B.C. Eraclius² describes the manufacture of lead glass as follows:

"Take good shining lead and put it into a new jar and burn it in the fire until it is reduced to a powder then take it away from the fire to cool; afterward take sand and mix with the powder, but so that two parts may be of lead and the third of sand, and put it into an earthen vase, then do as before directed for making glass."

Beckman² tells of an ancient mirror said to have belonged to Virgil, which was accidentally broken. One small piece, when analyzed, "showed that a considerable quantity of lead was used in the manufacture of the glass." "The earliest glass objects so far known date from the middle of the third millenium B.C., at the earliest, and all have been found in western Asia (Mesopotamia, Syria, etc.). They are small, solid objects such as beads, rods, and so forth; the earliest vessels from the same general area are dated on archeological grounds no earlier than the early 16th or 15th century B.C."³ All of these were opaque, translucent, or strongly colored.

Cristallo, or colorless glass, was developed by the Venetians before the middle of the 15th century, but in reality this was slightly brown or gray tinted. George Ravenscroft of London, by 1676, produced a lead crystal which "in transparency and brilliance came near to crystal."³ By the end of the 18th century, English lead crystal was the most sought-after glass in the world.³ One of the three known Ravenscroft goblets is on display at the Corning Museum of Glass.

Enameling of glass and metals is an ancient art form, initially used only for decorative purposes. Brightly colored lead-containing glass, melting at temperatures below that of the vessel to which it was to be applied, was ground to a powder and mixed into a suitable medium, such as an oil. This mixture was then painted onto the surface of the object to be decorated and fired. This procedure, seemingly a reasonable advancement over the earlier process of decoration with threads of brightly colored glass, was used to decorate gold, silver, copper, and bronze jewelry as well as glass. Enameling was well-known in Rome, Egypt, and Syria as early as the first century A.D.

Enameled glassware was manufactured in large quantity in Europe, especially Venice and Germany, from the 16th century onward.³ Enameled objects of gold, silver, and copper were also very popular. It was not until the early 1800's that enameling of cast iron for bathtubs was developed, with enameling of sheet steel following in about 1850.⁴

Lead, in the form of the oxide, has found an essential place in the manufacture of ceramic products because of many inherent properties essential to these processes and products. The great range of desirable properties, important not only in the melting and forming of glass and the firing of glazes and enamels, but also in the properties of the finished products, will be described in detail in later chapters. Lead oxide is an extremely versatile material that has held its place in ceramics for thousands of years, simply because no other material or combination of materials performs as well.

The proliferation of ceramic products through the centuries has greatly expanded the uses of lead in the form of the monoxide in ceramic products. This is true of the past 100 years, especially since the invention of incandescent

and fluorescent lighting, television, the computer, and the host of other electronic inventions and developments, requiring nearly 80 000 tons per year of lead oxide.

This book is presented in an effort to provide, in one cover, as much of today's knowledge of the ceramic applications of lead compounds as is known to us at this time. The ancient background information is essential for perspective, along with the new research, which has grown greatly in volume in recent years. We will not attempt to extrapolate to future years, but we are confident that the future holds much in the way of exciting and invaluable developments, made possible by the properties of this exceedingly versatile material, lead oxide.

Production of lead may rival that of pottery in its antiquity. While those activities are not the oldest profession, the production of lead may well be the oldest industry.

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1

Lead Compounds and Their Properties

Four general types of lead chemicals are manufactured for ceramic use. These are litharge, red lead, white lead, and the lead silicates. Several variations of each product are prepared so that each may be adapted to a wide variety of uses.

Litharge (Lead Monoxide-PbO)

Litharge is the basic unit in the chemistry of lead in ceramics. Whatever the compound may be, the portion of principal interest is PbO. Litharge, of course, is 100% PbO. It is the simplest of the lead compounds.

Litharge is used in the manufacture of glass, dry process enamels, and in the production of frits for all purposes. It is manufactured by the oxidation of metallic lead by a variety of processes, each resulting in a distinctive variation in physical properties. As a result, litharge is available in a wide range of particle sizes and in two crystal forms.

The yellow or orthorhombic form is stable at temperatures between about 550 and 888°C (1022 and 1630°F), the melting point. It is metastable at normal temperature. The red or tetragonal crystal form results from oxidation of lead at temperatures around the melting point of lead and below the range where red lead (Pb_3O_4) is formed. A red modification of litharge is formed also when molten litharge is allowed to cool slowly. In this case, it forms a flaky form of tetragonal litharge. When fused litharge is chilled rapidly, it crystallizes in the orthorhombic system, but usually as a flaky variety.

Sublimed or fumed litharge is typical of the orthorhombic form. Most mechanical furnace litharge is formed first in the yellow form but is converted partially to the red form by attrition during the milling operation. This partial conversion alters the color from bright yellow to a slightly tan shade.

The crystal form of litharge, so far as is known, is not of great importance in its use in ceramic processes. It is well, however, to recognize these differences because of the frequent questions in this regard. In processes involving aqueous reactions, the yellow form is much more reactive than the red.

Apparent density, particle size, and chemical purity are the important criteria when litharge is being selected for a specific use in a ceramic process. Apparent density and particle size are determined by the method of manufacture. Extreme purity is quite typical of contemporary manufacturing methods. It is the result largely of starting with pure metallic lead and the use of great care in processing, handling, and packing to prevent contamination.

Purity requirements become more demanding with passing time and new developments. While up to 5 ppm of coloring oxide impurity was considered

Properties		Litharge						
Sublimed or tumbled	Milled	Screened	Granular	Red lead	White lead	Lead monosilicate	Lead bisilicate	Tribasic lead silicate
Composition	PbO	PbO	PbO	Pb ₃ O ₄	2PbCO ₃ · Pb(OH) ₂	PbO · 0.67SiO ₂	PbO · 0.03Al ₂ O ₃ · 1.95SiO ₂	PbO · 0.254Al ₂ O ₃ · 1.91OSiO ₂
Apparent molecular weight	223.21	223.21	223.21	685.63	775.67	263.27	343.47	363.82
Equivalent weight	223.21	223.21	223.21	228.54	258.56	263.27	343.47	243.27
Specific gravity	9.65	9.55	9.4-9.5	8.95-9.10	6.8	6.50-6.65	4.60-4.65	363.82
Apparent density								7.52
Scott volumeter (g/in. ³)	30-40	50-80	70-80	20-25	7-9			
Packing weight (lb./ft. ³)	90-100	280-350	280-350	210-230	90-100	200-230	170-200	160-190
Melting range: °F	1630	1630	1630	1020 decomposes	730 decomposes	1250-1350	1450-1500	1425-1475
Melting range: °C	888	888	888	550 decomposes	390 decomposes	677-732	788-816	774-802
Coefficient of linear thermal expansion (50-450°C)								
Color	yellow	yellow	reddish yellow	orange-red	white	9.3 × 10 ⁻⁶	7.1 × 10 ⁻⁶	5.9 × 10 ⁻⁶
Refractive index	2.67					light yellow	light yellow	light yellow
Solubility in water	slight	slight	slight	insoluble	slight	2.00-2.02	1.72-1.74	insoluble
	99%	varies	usually	99%	99%	insoluble	insoluble	insoluble
	-325 mesh	-325 mesh	-10 mesh	-325 mesh	-325 mesh	95-99%	95%	95%
Screen analysis						-10 mesh	-10 mesh	-10 mesh
						granular	granular	granular
						95% - 200 mesh	95% - 200 mesh	95% - 200 mesh
						ground	ground	ground
						95% - 325 mesh		

quite good only a few years ago, some new developments now require purity levels measured in a low number of parts per billion. Needless to say, such purity levels are attained at high cost, far removed from the cost of volume commercial lead products.

Red Lead (Pb_3O_4)

Red lead is manufactured by further oxidation of litharge. In this process litharge is roasted at a temperature near 482°C (900°F). The oxidation of the litharge particles proceeds from the surface toward the center and reaches a degree of completion within a given time which is largely dependent on the particle size of the litharge used. Ceramic grades of red lead by choice are usually quite dense with relatively large particle size. The true Pb_3O_4 content is about 75%, the balance being PbO .

Among the merits of red lead is the fact that the extra oxygen that it contains is released at about 550°C (1020°F). Thus, red lead provides an important measure of protection against reduction during the early stages of melting of lead glasses.

Lead Silicates

Probably the most versatile of lead compounds are the lead silicates. They are manufactured in granular, dustless, free-flowing form for use in glass, dry process enamels, and in frit batches, or in finely divided preground form for use in glazes or in certain ceramic bodies. They are, therefore, adaptable for almost any conceivable use by the ceramic industries.

Three types of silicates are available commercially. These are considered separately.

Lead Monosilicate ($\text{PbO} \cdot 0.67\text{SiO}_2$)

This composition contains 85% PbO and 15% SiO_2 . It is approximately the eutectic mixture of lead orthosilicate ($2\text{PbO} \cdot \text{SiO}_2$) and lead metasilicate ($\text{PbO} \cdot \text{SiO}_2$). The name is therefore not accurately descriptive of the composition. In finely powdered form, it is readily soluble in dilute hydrochloric or acetic acid.

Lead Bisilicate ($\text{PbO} \cdot 0.03\text{Al}_2\text{O}_3 \cdot 1.95\text{SiO}_2$)

This material, also known as lead aluminum bisilicate, contains 65% PbO , 1% Al_2O_3 , and 34% SiO_2 . While its principal use at this time is in pottery and wall tile glazes, a new and growing use is developing in low-temperature bodies and in some of the ultralow-loss dielectric bodies. Lead bisilicate is also used in the manufacture of reflective spheres for highway marking and sign use.

Other lead aluminum bisilicates are also available from frit manufacturers, of which the cone deformation eutectic composition is an example. This composition is $\text{PbO} \cdot 0.254\text{Al}_2\text{O}_3 \cdot 1.910\text{SiO}_2$, containing 61.35% PbO , 7.12% Al_2O_3 , and 31.53% SiO_2 .

Lead bisilicates are extremely resistant to leaching by dilute acids, including gastric juice. For this reason, this type of composition greatly reduces toxic properties and offers the maximum of safety of any of the lead products.

Tribasic Lead Silicate ($\text{PbO} \cdot 0.33\text{SiO}_2$)

This highly basic lead silicate is manufactured only in granular form and is intended only for use in lead glass where bulk shipping, storing, and handling methods are used. It contains 92% PbO and 8% SiO_2 and is the eutectic of tetralead silicate ($4\text{PbO} \cdot \text{SiO}_2$) and lead orthosilicate ($2\text{PbO} \cdot \text{SiO}_2$). The powdered form is readily soluble in dilute acids.

In general, the lead silicates are manufactured in highly pure form. The process in use is that of fusion of a mixture of very pure litharge and selected glass sand. Kaolin or pyrophyllite may be used as the source of Al_2O_3 in lead aluminum bisilicates. Mixed batch is usually fed continuously into a melting furnace. The fused lead silicate is usually quenched in water and dried. It may be ground before packing in bags or it may be shipped in granular form, either packed in bags or shipped in bulk in covered hopper cars, bulk trucks, or in portable bins, cartons, or "sling bins" holding 2000–3000 lbs (907–1361 kg).

White Lead ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$)

Basic carbonate white lead is manufactured by chemical precipitation from a slurry of litharge in water containing a small amount of acetic acid. Carbon dioxide gas is fed in carefully controlled amount and rate into a closed vessel under agitation. The resulting product is very pure, clean, white, and finely divided. With median particle radius of $0.35 \mu\text{m}$, it has excellent suspension qualities. The particles are sufficiently fine to be kept in constant agitation by Brownian movement in spite of the specific gravity of 6.9. See Fig. 1 for thermogram for basic carbonate white lead and decomposition products.

While basic carbonate white lead has a history of use in ceramics, especially in glazes, spanning many centuries, its use has been greatly diminished in recent years. White lead is readily soluble in many acid solutions, including gastric juice. In contrast, lead bisilicate and some of the pottery glaze frits are relatively insoluble and, therefore, present substantially less hazard to those who handle glaze materials in the plant. There remain, however, special circumstances where white lead is preferred and special precautions are taken to assure safety.

Lead Isotopes

Studies of the ratios of the four stable isotopes of lead (204, 206, 207, 208) present in lead ores from different mining areas has been helpful in the study of archaeological artifacts which contain lead. The distinctive patterns of isotopes in lead mined in various locations has made it possible, in many cases, to determine the sources of lead in ancient glass, glazes, and ancient metallic artifacts.

Robert H. Brill, Administrator of Scientific Research, Corning Museum of Glass, and associates have studied isotope ratios of lead ores and metals from many sources about the world. Similar studies of lead present in ancient artifacts, including metal goods, glass, glazed pottery, and tile have yielded extremely interesting information.

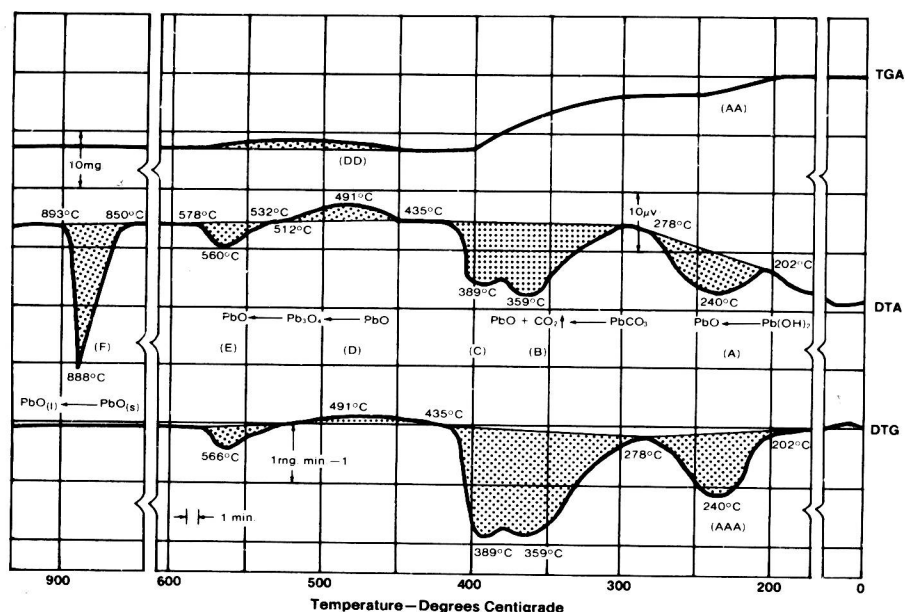


Fig. 1. Thermogravimetric analysis and differential thermal analysis diagrams for basic carbonate white lead and decomposition products. The DTA endotherm in the range 202 to 278°C (A) indicates the change from hydrous basic lead carbonate to the anhydrous form. This reaction may be represented as $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2 \rightarrow 2\text{PbCO}_3 \cdot \text{PbO} + \text{H}_2\text{O} \uparrow$. The loss of weight and rate are shown on the TGA and DTG plots (AA) and (AAA). At 359 and 389°C, (B) and (C), there are two endotherms, with accompanying loss of weight indicating a two-stage decomposition of anhydrous basic lead carbonate to lead monoxide in the tetragonal state. This might be represented as $2\text{PbCO}_3 \cdot \text{PbO} \rightarrow \text{PbCO}_3 \cdot 2\text{PbO} + \text{CO}_2 \uparrow \rightarrow 3\text{PbO} + \text{CO}_2 \uparrow$. Upon continued heating of the material, the DTA exotherm at 435 to 532°C (D) and thermogravimetric weight gain (DD), show the oxidation of lead monoxide to red lead. There follows the decomposition of the red lead to lead monoxide in the orthorhombic state (yellow), as evidenced by the endotherm at 532 to 578°C (E). Lead monoxide melts at 888°C (F), as indicated by the endotherm peak.

We feel that reference to this work and to the writings of R. H. Brill et al. is of value to some of our readers.

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