1. Introduction

Lead (qv) is a member of Group 14 (IVA) of the Periodic Table because it has four electrons in its outer, or valence, shell. However, the usual valence of lead is +2, rather than +4. The two *s* electrons have higher ionization energies. As a result, tetravalent lead exists as a free, positive ion only in minimal concentrations. Furthermore, the bivalent or plumbous ion differs from the other Group 14 bivalent ions, such as the stannous ion of tin, because Pb^{2+} does not have reducing properties.

In general, the chemistry of inorganic lead compounds is similar to that of the alkaline-earth elements. Thus the carbonate, nitrate, and sulfate of lead are isomorphous with the corresponding compounds of calcium, barium, and strontium. In addition, many inorganic lead compounds possess two or more crystalline forms having different properties. For example, the oxides and the sulfide of bivalent lead are frequently colored as a result of their state of crystallization. Pure, tetragonal α -PbO is red; pure, orthorhombic β -PbO is yellow; and crystals of lead sulfide, PbS, have a black, metallic luster.

The carbonates, sulfates, nitrates, and halides of lead (except the yellow iodide) are colorless. Bivalent lead forms a soluble nitrate, chlorate, and acetate; a slightly soluble chloride; and an insoluble sulfate, carbonate, chromate, phosphate, molybdate, and sulfide. Highly crystalline basic lead salts of both anhydrous and hydrated types are readily formed. Tetrabasic lead sulfate [52732-72-6], 4PbO · PbSO₄, and the hydrated tribasic salt [12397-06-7], 3PbO · PbO₄ · H₂O, for example, may be formed by boiling suspensions of lead oxide and lead sulfate in water. In addition, complex mixed salts, such as white lead, $2PbCO_3 \cdot Pb(OH)_2$, are readily formed.

A clean lead surface is not attacked by dry air, but in moist air the surface quickly becomes coated with a film of lead monoxide, PbO, which may be hydrated and quickly combine with carbon dioxide from the atmosphere to produce a lead carbonate. Most of this combined carbon dioxide can be driven off by heating to 250° C, but traces remain even after heating to higher (650° C) temperatures for long periods. The ease with which lead monoxide combines with silicon dioxide to form a low melting silicate has been utilized in the ceramics industry in the preparation of glazes and in the manufacture of certain types of glasses (see GLASS-CERAMICS; SILICON COMPOUNDS).

Tetravalent lead is obtained when the metal is subjected to strong oxidizing action, such as in the electrolytic oxidation of lead anodes to lead dioxide, PbO₂; when bivalent lead compounds are subjected to powerful oxidizing conditions, as in the calcination of lead monoxide to lead tetroxide, Pb_3O_4 ; or by wet oxidation of bivalent lead ions to lead dioxide by chlorine water. The inorganic compounds of tetravalent lead are relatively unstable; eg, in the presence of water they hydrolyze to give lead dioxide.

The lead storage battery, the largest single user of lead and its compounds, is made possible by the high degree of reversibility, both chemical and physical, in the fundamental chemical reaction

$$Pb + PbO_2 + 2 H_2SO_4 \Longrightarrow 2 PbSO_4 + 2 H_2O_4$$

The reaction is especially useful because of the high emf (ca 2.2 V) of the Pb/PbO₂ couple in dilute sulfuric acid (see BATTERIES, SECONDARY).

All lead-containing compounds are produced from pig lead through a series of suitable steps, except for the small amount of lead in leaded zinc oxide for which high grade lead ore is used. Most lead compounds are prepared directly or indirectly from lead monoxide, PbO, commonly known as litharge. The physical nature of the oxide, as to particle size, and its exact method of preparation have profound effects on the suitability of any particular lead monoxide product for use in any specific process. In general, lead compounds may be formed by one or more of three methods: (1) reaction between a slurry of litharge, or a similar lead compound such as the hydroxide or carbonate, and the desired acid, or solution thereof in the case of an organic acid, or soluble salt of that acid; (2) reaction between the solution of a lead salt and the desired acid, or solution thereof in the case of an organic acid, or soluble salt of the acid. These reactions are facilitated by the fact that the desired lead compound usually is relatively insoluble, thus forming as a precipitate; and (3) fusion or calcination of litharge and the desired oxide, such as B₂O₃, SnO₂, ZrO₂, and TiO₂, resulting in lead borate, lead stannate [1344-41-8], lead zirconate, ZrO₂, and lead titanate. This method is particularly applicable with the oxides of the elements in Groups 14 (IVA), 15 (VA), and 16 (VIA) of the Periodic Table.

Most uses of lead in chemical compounds other than in storage batteries are dissipative. The greater part of the lead used in other forms is recoverable.

2. Lead Halides

2.1. Lead Fluoride. Lead diffuoride, PbF_2 , is a white orthorhombic salt to about 220°C where it is transformed into the cubic form; some physical properties are given in Table 1. Lead fluoride is soluble in nitric acid and insoluble in acetone and ammonia. It is formed by the action of hydrofluoric acid on lead hydroxide or carbonate, or by the reaction between potassium fluoride and lead nitrate.

Lead fluoride has been used in low power fuses (1), as a catalyst for the manufacture of picoline (see Pyridines and pyridine derivatives) (2), in glass coatings for infrared reflection (3), in low melting glasses (4), in phosphors for television-tube screens (see LUMINESCENT MATERIALS) (5), in activators for electroless plating (qv) of nickel on glass (6), in electrooptical coatings (7), and in zinc oxide varistors (8).

2.2. Lead Tetrafluoride. Like all the lead tetrahalides, lead tetrafluoride [7783-59-7],PbF₄, is very reactive. It is relatively the most stable halide, however. PbF₄ is a white crystalline powder which is highly moisture sensitive, turning yellowish brown in moist air owing to hydrolysis. It should be handled in a dry box or under an atmosphere of dry nitrogen. Properties for PbF₄ are in Table 1.

 PbF_4 , produced by various routes including the *in situ* species, is a very effective fluorinating agent and also an oxidizing agent. It is classified as a hard fluorinating agent (9), replacing hydrogen with fluorine or adding fluorine

to double bonds of both halogenated and hydrocarbon olefins to produce diffuorocarbons (10,11).

$$CCl_2 = CCl_2 + PbF_4 \longrightarrow CCl_2FCCl_2F + PbF_2$$
(1)

$$CF_3CCl = CCl_2 + PbF_4 \longrightarrow CF_3CClFCCl_2F + PbF_2$$
(2)

$$CHCl = CHCl + PbF_4 \longrightarrow CHClFCHClF + PbF_2$$
(3)

It is also used in the preparation of biologically active steroids where the fluorine is added in a cis configuration to the double bond (12,13).

2.3. Lead Chloride. Lead dichloride, $PbCl_2$, forms white, orthorhombic needles; some physical properties are given in Table 1. Lead chloride is slightly soluble in dilute hydrochloric acid and ammonia and insoluble in alcohol. It is prepared by the reaction of lead monoxide or basic lead carbonate with hydrochloric acid and allowing the precipitate to settle. It easily forms basic chlorides, such as $PbCl_2 \cdot Pb(OH)_2$ [15887-88-4], which is known as Pattinson's lead white, an artist's pigment.

Lead dichloride is the starting material for a number of organolead compounds (14). It has been used in asbestos clutch or brake linings (see BRAKE LININGS AND CLUTCH FACINGS) (15), as a co-catalyst for acrylonitrile production (16), as a catalyst for polymerization of olefins to highly crystalline, stereoregular polymers (17), as a cathode for magnesium-lead dichloride seawater batteries (18), to make rectifying junctions on gallium arsenide (19), as a flame retardant in polycarbonates (20) and nylon-6,6 wire coatings (21), as a flux for the galvanizing of steel (22), as a solid-phase chemical scrubber for ozone and hydrogen sulfide removal from gas (23), as a photochemical-sensitizing agent for metal patterns on printed circuit boards (24), and as a sterilization indicator on tapes that darken with zinc sulfide at 121° C in moist air (25).

2.4. Lead Bromide. Lead dibromide, PbBr₂, forms white orthorhombic crystals; some physical properties are given in Table 1. Lead(II) bromide is slightly soluble in ammonia and highly soluble in potassium bromide solutions owing to complex formation, soluble in acetic acid, but insoluble in alcohol. On exposure to light, lead dibromide decomposes slowly and darkens because of release of lead. It is prepared from lead monoxide or carbonate and hydrobromic acid, or lead diiodide and lead(IV) bromide, or by treating an aqueous solution of lead nitrate with hydrobromic acid or a soluble metal bromide and allowing the precipitate to settle.

Lead bromide is a photopolymerization catalyst for acrylamide monomer and is used in photoduplication at exposures of 365-nm radiation (26). Blackgray positive images are obtained on a white background by applying a methyl alcohol solution of lead bromide in a poly(vinyl butyral) binder to a suitable substrate and then exposing the coating to light through a negative film (27). In another photographic process, the latent image is developed by reduction of PbBr₂ with a sulfur-containing reducing agent, such as mercaptoacetic acid (28). Lead dibromide used as an inorganic filler in fire-retardant polypropylene, polystyrene, and acrylonitrile-butadiene-styrene (ABS) plastics reduces the

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requirements of chlorinated hydrocarbon flame-resistant additives (29) (see FLAME RETARDANTS). For welding (qv) aluminum or aluminum-base alloys to other metals, such as iron, nickel, copper, zinc, or their alloys, an aqueous paste containing PbBr₂ serves as an excellent general-purpose welding flux (30).

2.5. Lead lodide. Lead diiodide, PbI_2 , forms a powder of yellow hexagonal crystals; some physical properties are given in Table 1. Lead diiodide is soluble in alkalies and potassium iodide, and insoluble in alcohol. It is made by treating a water-soluble lead compound with hydroiodic acid or a soluble metal iodide. It is readily purified by recrystallization in water.

Lead iodide decomposes when exposed to green light at about 180° C, thereby making it possible to record optical images on thin lead iodide films (31). other applications of lead iodide include photographic emulsions with thiols (32), aerosols for cloud seeding to produce rain artificially (33), asbestos brake linings (34), primary thermal batteries with iodine (35), mercury-vapor arc lamps (36,37), thermoelectric materials (38,39), lubricating greases (40), electrosensitive recording papers (41), and filters for far-infrared astronomy (42).

3. Oxides

Lead forms two simple oxides, PbO and PbO₂, where it is divalent and tetravalent, respectively. Lead also forms a mixed oxide, Pb_3O_4 , and a black oxide which normally comprises 55–85% lead monoxide, the remainder being finely divided metallic lead. The largest market for lead chemicals is the use of lead oxides in lead-acid storage battery electrodes (see BATTERIES, SECONDARY). The ceramics industry is the next largest consumer of lead oxides, for use in glasses, glazes, and vitreous enamels for metal coating and glass decoration (see CERAMICS), followed by the rubber industries. Lead also forms reacted mixed oxides with other metals, eg, the ferrites (qv), useful as ferrimagnetic materials, and the titanates or zirconates, which are ferroelectric materials (see FERROELECTRICS). Lead monoxide, PbO, is used widely as a component of heat stabilizers (qv) (basic lead salts) for poly(vinyl chloride) resins (43). Some physical properties of lead oxides are given in Table 2.

Total consumption of lead in the United States in 2003 reached $1,460 \times 10^3$ t. Of this, 80% is allocated to battery use supplied as either a mixed oxide or as metal. Approximately 97% of batteries are recycled and the lead recovered (44).

In 2003 the Battery Council announced that for the period 1997–2001 the lead recycling rate ranked higher than any other recyclable materials.

In 2003, transportation industries were the principal users of lead, consuming 76% of it for batteries, solder, seals, bearings, and wheel weights. Electrical, electronic and communication devices (including batteries), ammunition, television glass, construction materials and protective coatings accounted for 22% of consumption. The remainder was used in ballast and counterweights, ceramics and glass, tubes and containers, type metal, foil, wire, and specialized chemicals (44).

3.1. Lead Monoxide. Lead monoxide (litharge), PbO, occurs as a reddish alpha form, which is stable up to 489°C where it transforms to a yellow beta form (massicot). The latter is stable at high temperatures. The solubility of α -PbO in water is 0.0504 g/L at 25°C; the solubility of the β -PbO is 0.1065 g/L at 25°C (45). Lead monoxide is amphoteric and dissolves in both acids and alkalies. In alkalies, it forms the plumbite ion PbO₂^{2–}. The monoxide is produced commercially by the reaction of molten lead with air or oxygen in a furnace. Black or gray oxide is manufactured by the Barton process, by the oxidation of atomized molten lead in air, as well as by the ball mill process, in which metallic lead balls of high purity are tumbled in the mill to form partially oxidized lead particles.

Lead monoxide is used primarily as plates for electric storage batteries of the lead-sulfuric acid type. It is also widely used in optical, electrical, and electronic glasses, as well as in the glazing of fine tableware. For use in glazes and vitreous enamels, lead oxides are often converted to lead mono-, bi-, and trisilicate frits to render the lead compounds insoluble (see ENAMELS, PORCELAIN OR VITREOUS). Litharge is also used in rubber and plastics as a vulcanizing agent; in lead soaps employed in the past as driers in varnishes; as a high temperature lubricant; as a neutralizing agent in organic syntheses; and as an intermediate material in the manufacture of pigments (46).

3.2. Lead Dioxide. Lead dioxide (lead peroxide, plattnerite), PbO₂, is a brownish black crystalline powder consisting of fine crystalline flakes in either α -or β - form. Lead dioxide decomposes rather easily to the lower oxide, releasing oxygen when heated to 290°C and above. It is practically insoluble in water or alkaline solutions, slowly soluble in acetic acid or ammonium acetate, and more rapidly soluble in hydrochloric acid and in a mixture of nitric acid and hydrogen peroxide. Lead dioxide can be produced by anodic oxidation of solutions of lead salts or, commercially, by the oxidation of red lead, Pb₃O₄, in alkaline slurry with chlorine.

Lead dioxide is electrically conductive and is formed in place as the active material of the positive plates of lead-acid storage batteries. Because it is a vigorous oxidizing agent when heated, it is used in the manufacture of dyes, chemicals, matches (qv), pyrotechnics (qv), and liquid polysulfide polymers (47) (see POLYMERS CONTAINING SULFUR).

3.3. Lead Sesquioxide. Lead sesquioxide (lead trioxide), Pb_2O_3 , is an amorphous, orange-yellow powder soluble in cold water. It decomposes in hot water and in acids to lead salts plus PbO₂. Lead sesquioxide can be prepared from lead dioxide by hydrothermal dissociation (48).

Lead sesquioxide is used as an oxidation catalyst for carbon monoxide in exhaust gases (49,50) (see EXHAUST CONTROL), as a catalyst for the preparation of lactams (51) (see β -LACTAMS), in the manufacture of high purity diamonds (52) (see DIAMOND, NATURAL), in fireproofing compositions for poly(ethylene terephthalate) plastics (53), in radiation detectors for x-rays and nuclear particles (54), and in vulcanization accelerators for neoprene rubber (55).

3.4. Lead Tetroxide. Lead tetroxide (red lead; minium; lead orthoplumbite), Pb_3O_4 , is a brilliant orange-red pigment which accounted for U.S. shipments of 17,780 t in 1977, mainly to the ceramics and storage battery industries. U.S. shipments in 2002 of red and white lead amounted to approximately 20,400 t (56). It is insoluble in water and alcohol, and dissolves in acetic acid or hot hydrochloric acid. Red lead is manufactured by heating lead monoxide

in a reverberatory furnace in the presence of air at $450-500^{\circ}$ C until the desired oxidative composition is obtained.

Red lead was used as a pigment in anticorrosion paints for steel surfaces (57,58), such as bridges (59) and reinforcements of concrete (60), and in adhesives for polyester tire cords (61). It continues to be used in positive battery plates (62), in colored glass for fiber optics (qv) (63), in electrically conductive polymer compositions (64), in catalysts for combustion of carbon monoxide in exhausts (65), in explosives for metal forming (66), in photochromic glass (see CHROMOGENIC MATERIALS) (67), in low melting glass-ceramics (68), in propellants for inflation of automotive safety bags (69,70), in radiation shields for gamma rays (71), in the vulcanization of polyether rubbers (72), in sealing glasses for color television picture tubes (73), in foaming agents for porcelain building materials (74), as an inhibitor of zinc dendrite growth in alkaline storage cells (75), in rubber sheets for x-ray protection (76), and in waterproofing putty for ship hulls (77).

3.5. Lead Hydroxide. Lead hydroxide [19781-14-3], Pb(OH)₂, mol wt 241.23, starts to dehydrate at about 130° C, and decomposes to lead monoxide at 145°C. It is only sparingly soluble in water (0.0155 g/100 mL at 20°C; slightly more in hot water), soluble in acids and alkalies, but insoluble in acetone. Lead hydroxide is prepared by adding alkali to a solution of lead nitrate or by electrolysis of an alkaline solution with a lead anode.

Lead hydroxide is used in sealed nickel-cadmium battery electrolytes (78), in oxidation catalysts for cyclododecanol (79), in electrical insulating paper (80), in gel stabilizers for petroleum well plugging (81), in the manufacture of porous glass (82), in wastewater filters for chromate removal (83), in building radiation shielding (84), in lubricating grease (85), with a thiourea derivative in photothermographic copy sheets (86), and in uranium recovery from seawater (87).

4. Lead Sulfide

Lead sulfide [1314-87-0] (galena, lead glance), PbS, mol wt 239.25, mp 114°C, d = 7.57 - 7.59 g/cm³, is metallic black and crystallizes in the cubic system. It has a hardness of 2.5–2.75 on the Mohs' scale. Lead sulfide is sparingly soluble in water (0.01244 g/100 mL at 20°C), but dissolves easily in dilute nitric acid where the sulfur is oxidized to the elemental state. Concentrated hydrochloric acid decomposes lead sulfide, liberating hydrogen sulfide. Lead sulfide is photoconductive. It is the chief ore of lead and is prepared by heating metallic lead in sulfur vapor. It is available in technical and high purity (99.999%) grades.

Lead sulfide is used in photoconductive cells, infrared detectors, transistors, humidity sensors in rockets, catalysts for removing mercaptans from petroleum distillates, mirror coatings to limit reflectivity, high temperature solid-film lubricants, and in blue lead pigments (88).

5. Lead Telluride

Lead telluride [1314-91-6], PbTe, forms white cubic crystals, mol wt 334.79, sp gr 8.16, and has a hardness of 3 on the Mohs' scale. It is very slightly soluble in water, melts at 917°C, and is prepared by melting lead and tellurium together. Lead telluride has semiconductive and photoconductive properties. It is used in pyrometry, in heat-sensing instruments such as bolometers and infrared spectroscopes (see INFRARED TECHNOLOGY AND RAMAN SPECTROSCOPY), and in thermoelectric elements to convert heat directly to electricity (38,39,89). Lead telluride is also used in catalysts for oxygen reduction in fuel cells (qv) (90), as cathodes in primary batteries with lithium anodes (91), in electrical contacts for vacuum switches (92), in lead-ion selective electrodes (93), in tunable lasers (qv) (94), and in thermistors (95).

6. Lead Sulfates

Lead forms a normal and an acid sulfate and several basic sulfates. Basic and normal lead sulfates are fundamental components in the operation of leadsulfuric acid storage batteries. Basic lead sulfates also are used as pigments and heat stabilizers (qv) in vinyl and certain other plastics.

6.1. Lead Sulfate. Lead sulfate, $PbSO_4$, is soluble in concentrated acids and alkalies, forming hydroxyplumbites; some physical properties are given in Table 3. It is prepared by treating lead oxide, hydroxide, or carbonate with warm sulfuric acid, or by treating a soluble lead salt with sulfuric acid. Lead sulfate forms in lead storage batteries during discharge cycles. It has been used in photography in combination with silver bromide and is used in the stabilization of clay soil for adobe structures, earth-fill dams, and roads (96).

6.2. Monobasic Lead Sulfate. Monobasic lead sulfate, PbO · PbSO₄, is very slightly soluble in hot water and slightly soluble in sulfuric acid; some physical properties are given in Table 3. Basic lead sulfate can be prepared by fusing PbO and PbSO₄ or by boiling aqueous suspensions of these two components. The resultant white solid is filtered and dried. It is available in 225-kg multiwall bags. Basic lead sulfate is used in paints as a white pigment, in poly(vinyl chloride) (PVC) plastics as a heat stabilizer, in rubbers as an inert filler, and as additives in textile dyeing and printing (97).

6.3. Dibasic Lead Sulfate. Dibasic lead sulfate [12036-76-9], $2PbO \cdot PbSO_4$, is a white powder, mol wt 749.70, mp 961°C. The dibasic compound can be prepared by fusion of the two components. It has been sold as a PVC stabilizer in Japan and is sold in Europe in combination with dibasic lead phosphite.

6.4. Tribasic Lead Sulfate. Tribasic lead sulfate [12202-17-4], $3PbO \cdot PbSO_4 \cdot H_2O$, is a fine white powder, mol wt 890.93, sp gr 6.9, refractive index 2.1, lead oxide content 90.1%, sieve analysis, 99.8% through 44 µm (325 mesh) (wet), water solubility 0.0262 g/L at 18°C. Tribasic lead sulfate is by far the most widely used basic lead sulfate for the stabilization of PVC polymers. It may be prepared by boiling aqueous suspensions of lead oxide and lead sulfate. The anhydrous compound decomposes at 895°C. Tribasic lead sulfate

provides efficient, long-term heat stability in both flexible and rigid PVC compounds, it is easily dispersible and has excellent electrical insulation properties, and it is an effective activator for azodicarbonamide-type blowing agents for vinyl foams. Applications for tribasic lead sulfate stabilizers include thermal stabilization of flexible PVC wire insulation compounds containing phthalate-type plasticizers, wire insulation designed to meet Underwriters' Laboratories specifications through 80°C, rigid and flexible PVC foams, rigid vinyl profiles, and PVC plastisols. The usual range of tribasic lead sulfate required in PVC is between two and seven parts per hundred of resin (2–7 phr), depending on the intended application of the vinyl product.

6.5. Tetrabasic Lead Sulfate. Tetrabasic lead sulfate [12065-90-6], 4PbO · PbSO₄, mol wt 1196.12, sp gr 8.15, is made by fusion of stoichiometric quantities of litharge (PbO) and lead sulfate (PbSO₄); heat of formation, $\Delta H^{\circ} =$ -1814 kJ/mol (-434.1 kcal/mol). Alternatively, tetrabasic lead sulfate may be prepared by boiling the components in aqueous suspensions. At about 70°C, tribasic hydrate reacts with lead oxide to form tetrabasic sulfate. At 80°C, this transformation is complete in ~20 hours. Tetrabasic lead sulfate is used in limited quantities in Europe as a PVC stabilizer. However, in the United States, lead-acid batteries have been developed by Bell Telephone Laboratories, which contain tetrabasic lead sulfate. Such batteries are used for emergency power at telephone switchboard stations and have an anticipated service life of over 50 years.

7. Lead Nitrate

Lead nitrate [10099-74-8], Pb(NO₃)₂, mol wt 331.23, sp gr 4.53, forms cubic or monoclinic colorless crystals. Above 205°C, oxygen and nitrogen dioxide are driven off, and basic lead nitrates are formed. Above 470°C, lead nitrate is decomposed to lead monoxide and Pb₃O₄. Lead nitrate is highly soluble in water (56.5 g/100 mL at 20°C; 127 g/100 mL at 100°C), soluble in alkalies and ammonia, and fairly soluble in alcohol (8.77 g/100 mL of 43% aqueous ethanol at 22°C). Lead nitrate is readily obtained by dissolving metallic lead, lead monoxide, or lead carbonate in dilute nitric acid. Excess acid prevents the formation of basic nitrates, and the desired lead nitrate can be crystallized by evaporation.

Lead nitrate is used in many industrial processes, ranging from ore processing to pyrotechnics (qv) to photothermography. Thus lead nitrate is used as a flotation agent in titanium removal from clays (98); in electrolytic refining of lead (99); in rayon delustering (100); in red lead manufacture (101); in matches, pyrotechnics, and explosives (102); as a heat stabilizer in nylon (103); as a coating on paper for photothermography (104); as an esterification catalyst for polyesters (105); as a rodenticide (see PESTICIDES) (106); as an electroluminescent mixture with zinc sulfide (107); as a means of electrodepositing lead dioxide coatings on nickel anodes (108); and as a means of recovering precious metals from cyanide solutions (109).

8. Lead Phosphite

In commercial applications of poly(vinyl chloride) polymers where weathering resistance, thermal stability, and electrical insulating properties are required, a stabilizer system base on dibasic lead phosphite provides a unique balance of properties. Its plasticizer reactivity is in the same range as dibasic lead phthalate, its electrical properties are superior, and it is the only stabilizer known that can provide the required electrical properties and weathering resistance in the absence of carbon black pigmentation. A properly formulated PVC electrical insulation compound containing a dibasic lead phosphite stabilizer, in combination with rutile-type titanium dioxide, remains in serviceable condition for up to 20 years. This superior performance results from the high absorption of the ultraviolet portion of sunlight, as well as the antioxidant activity of the phosphite anion (see ANTIOXIDANTS). The high PbO content of this dibasic lead salt makes it a very effective acid acceptor for HCl during PVC processing.

8.1. Dibasic Lead Phosphite. Dibasic lead phosphite [12141-20-7], $2PbO \cdot PbHPO_3 \cdot \frac{1}{2}H_2O$, is a white crystalline powder, mol wt 742.63, sp gr 6.9, refractive index 2.25, lead oxide content 90.2%, sieve analysis, 99.8% through 44 µm (325 mesh) (wet), water solubility, nil. Fields of application for dibasic lead phosphite stabilizers in PVC include garden hose, flexible and rigid vinyl foams (as high temperature activator for azodicarbonamide-type blowing agents), coated fabrics, plastisols, electrical insulation, and extruded profiles for outdoor use. In general, at five parts per hundred of resin (5 phr), dibasic lead phosphite provides good heat stability and superior outdoor weathering properties in PVC. This stabilizer should be stored in closed containers, away from open flames, and at temperatures below 200°C. Exposure to sparks or static electricity should be avoided by grounding all electrical equipment and using wooden scoops.

9. Lead Azide

Lead azide [13424-46-9], Pb(N₃)₂, mol wt 291.23, crystallizes as colorless needles. It is a sensitive detonating agent, exploding at 350°C (see ExpLOSIVES; PROPEL-LANTS). Lead azide should always be handled and shipped submerged in water to reduce sensitivity. Its water solubility is very low (0.023 g/100 mL at 18°C and 0.09 g/100 mL at 70°C) and it is insoluble in ammonium hydroxide but very soluble in acetic acid. Lead azide is commonly prepared by the reaction between dilute solutions of lead nitrate and sodium azide. For safety, it is stirred vigorously to prevent formation of large crystals, which may detonate. Lead azide is usually precipitated with a protective material, such as gelatin, and then granulated (110). Lead azide is also used to prepare electrophotographic layers (111) and for information storage on styrene–butadiene resins (112).

10. Lead Antimonate

Lead antimonate [13510-89-9] (Naples yellow), $Pb_3(SbO_4)_2$, mol wt 993.07, $d = 6.58g/cm^3$, is an orange-yellow powder that is insoluble in water and dilute acids, but very slightly soluble in hydrochloric acid. Lead antimonates are modifiers for ferroelectric lead titanates, pigments in oil-base paints, and colorants for glasses and glazes (see COLORANTS FOR CERAMICS). They are made by the reaction of lead nitrate and potassium antimonate solutions, followed by concentration and crystallization.

11. Lead Acetates

11.1. Anhydrous Lead Acetate. Anhydrous lead acetate [301-04-2] (plumbous acetate), $Pb(C_2H_3O_2)_2$, is a white, crystalline solid that decomposes on heating above its melting point; some physical properties are given in Table 4. Because of its high solubility in water, lead acetate is often used for the preparation of other lead salts by the wet method. Lead acetate is made by dissolving lead monoxide (litharge) or lead carbonate in strong acetic acid. Several types of basic salts are formed when lead acetates are prepared from lead monoxide in dilute acetic acid or at high pH. The basic salts of lead acetate are white crystalline compounds, which are highly soluble in water and dissolve in ethyl alcohol.

11.2. Basic Lead Acetate. Basic lead acetate [1335-32-6] (lead subacetate), $2Pb(OH)_2 \cdot Pb(C_2H_3O_2)_2$, is a heavy white powder which is used for sugar analyses. Some physical properties are given in Table 4. Reagent grade is available in 11.3-kg cartons and in 45- and 147-kg fiber drums.

11.3. Lead Acetate Trihydrate. Lead acetate trihydrate [6080-56-4] (plumbous acetate trihydrate), $Pb(C_2H_3O_2)_2 \cdot 3H_2O$, is a white, monoclinic crystalline solid; some physical properties are given in Table 4. Upon heating it loses some of its water of crystallization, and after melting, decomposes at 200°C. The trihydrate is highly soluble in water but insoluble in ethyl alcohol. It has an intensely sweet taste, hence it is sometimes called sugar of lead, but it is poisonous. The trihydrate is made by dissolving lead monoxide in hot dilute acetic acid solution; on cooling, large crystals separate, sometimes up to 60-cm long.

Lead acetate trihydrate, the usual commercial form, is used in the preparation of basic lead carbonate and lead chromate, as a mordant in cotton dyes, as a reagent for the manufacture of lead salts of higher fatty acids, as a water repellant, as a component in combined toning and fixing baths for daylight printing papers, and as a means of treating awnings and outdoor furniture to prevent removal of mildew- and rot-proofing agents by rain or laundering. Other uses include preparation of rubber antioxidants; processing agent in the cosmetic, perfume, and toiletry industries; component of coloring agents for adhesives; and preparation of organic lead soaps as driers of paints and inks. The trihydrate is available in technical and reagent grades in 11.3-kg cartons, and 45- and 181-kg fiber drums.

11.4. Lead Tetraacetate. Lead tetraacetate [546-67-8] (plumbic acetate), $Pb(C_2H_3O_2)_4$, is a colorless, monoclinic crystalline solid that is soluble in chloroform and in hot acetic acid, but decomposes in cold water and in ethyl alcohol. Some physical properties are given in Table 4. Lead tetraacetate can be prepared by adding warm, water-free, glacial acetate acid to red lead, Pb_3O_4 , and subsequent cooling. The salt decomposes with the addition of water to give PbO_2 , but the yield can be improved by passing in chlorine gas. Lead tetraacetate is available in laboratory quantities as colorless to faintly pink crystals stored in glacial acetic acid.

Oxidation with lead tetraacetate is often used in organic syntheses, because the lead salt is highly selective in the splitting of vicinal glycols. The rate of oxidation of cis glycols is more rapid than of the trans isomers, a property widely used in the structural determination of sugars and other polyols. Lead tetraacetate readily cleaves α -hydroxy acids as oxalic acid at room temperature. Another use is the introduction of acetoxy groups in organic molecules, as in the preparation of cyclohexyl acetate and the acetoxylation of cyclohexanol. At high temperature, methylation takes place. In these reactions, the organic molecule must contain double bonds or activating substituents (113).

12. Lead Benzoate

Lead benzoate monohydrate [6080-57-5], $Pb(C_6H_5CO_2)_2 \cdot H_2O$, mol wt 467.43, is a white crystalline powder that loses its water of hydration when heated to 100°C. It is slightly soluble in cold water (0.16 g/100 mL at 20°C) and somewhat more soluble in warm water (0.31 g/100 mL at 49.5°C). The salt may be prepared by adding benzoic acid to a slurry of litharge, PbO, or by the reaction between solutions of sodium benzoate and a soluble lead compound. Lead benzoate is used as an antioxidant in organolead engine lubricants (114), as a catalyst in a blowing agent for polyethylene foams (115), and in fluorescence quenching of organic phosphors (116).

13. Lead Carbonates

13.1. Lead Carbonate. Lead carbonate [598-63-0], PbCO₃, mol wt 267.22, d = 6.6g/cm³, forms colorless orthorhombic crystals; it decomposes at about 315°C. It is nearly insoluble in cold water (0.00011 g/100 mL at 20°C), but is transformed in hot water to the basic carbonate, 2PbCO₃ · Pb(OH)₂. Lead carbonate is soluble in acids and alkalies, but insoluble in alcohol and ammonia. It is prepared by passing CO₂ into a cold dilute solution of lead acetate, or by shaking a suspension of a lead salt less soluble than the carbonate with ammonium carbonate at a low temperature to avoid formation of basic lead carbonate.

Lead carbonate has a wide range of applications. It catalyzes the polymerization of formaldehyde to high molecular weight crystalline poly(oxymethylene) products (117). It is used in poly(vinyl chloride) friction liners for pulleys on drive cables of hoisting engines (118). To improve the bond of polychloroprene to metals in wire-reinforced hoses, 10-25 parts of lead carbonate are used in the

elastomer (119). Lead carbonate is used as a component of high pressure lubricating greases (120), as a catalyst in the curing of moldable thermosetting silicone resins (121), as a coating on vinyl chloride polymers to improve their dielectric properties (122), as a component of corrosion-resistant, dispersionstrengthened grids in lead-acid storage batteries (123), as a photoconductor for electrophotography (qv) (124), as a coating on heat-sensitive sheets for thermographic copying (125), as a component of a lubricant-stabilizer for poly(vinyl chloride) (126), as a component in the manufacture of thermistors (127), and as a component in slip-preventing waxes for steel cables to provide higher wear resistance (128) (see COMPOSITE MATERIALS, POLYMER-MATRIX).

13.2. Basic Lead Carbonate. Basic lead carbonate [1319-46-6] (white lead), $2PbCO_3 \cdot Pb(OH)_2$, mol wt 775.67, $d = 6.14g/cm^3$, forms white hexagonal crystals; it decomposes when heated to $400^{\circ}C$. Basic lead carbonate is insoluble in water and alcohol, slightly soluble in carbonated water, and soluble in nitric acid. It is produced by several methods, in which soluble lead acetate is treated with carbon dioxide. For example, in the Thompson-Stewart process (129), an aqueous slurry of finely divided lead metal or monoxide, or a mixture of both, is treated with acetic acid in the presence of air and carbon dioxide. High quality, very fine particle-size basic lead carbonate is produced, ranging in carbonate content from 62 to 65% (vs 68.9% PbCO₃, theoretical).

Although white lead was the oldest white hiding pigment in paints, it has been totally replaced by titanium dioxide, which has better covering power and is nontoxic. Nevertheless, basic lead carbonate has many other uses, including as a catalyst for the preparation of polyesters from terephthalic acid and diols (130), a ceramic glaze component, a curing agent with peroxides to form improved polyethylene wire insulation (131), a pearlescent pigment (132), a color-changing component of temperature-sensitive inks (133), a red-reflecting pigment in iridescent plastic sheets (134), a smudge-resistant film on electrically sensitive recording sheets (135), a lubricating grease component (136), a component of ultraviolet light reflective paints to increase solar reflectivity (137), an improved cool gun-propellant stabilizer which decomposes and forms a lubricating lead deposit (138), a heat stabilizer for poly(vinyl chloride) polymers (139,140), and as a component of weighted nylon-reinforced fish nets made of poly(vinyl chloride) fibers (141).

14. Lead Phthalates

Two commercial forms of lead phthalates, both dibasic, are widely used as heat stabilizers (qv) in poly(vinyl chloride) (PVC) polymers and copolymers. During processing, usually extrusion, and in actual service, thermal degradation of PVC occurs principally by a dehydrochlorination mechanism. Thus one of the primary functions of dibasic lead phthalate stabilizers is to neutralize and inactivate the resulting hydrogen chloride. Such stabilizers are ideally suited for high temperature applications of PVC because of their low reactivity with plasticizers, particularly of the polyester type. Moreover, dibasic lead phthalates provide the long-term stability and retention of elongation required in 90 and 105°C Underwriters' Laboratories classes of wire insulation.

14.1. Dibasic Lead Phthalate. Dibasic lead phthalate [17976-43-1], $2PbO \cdot Pb(O_2C)_2C_6H_4 \cdot \frac{1}{2}H_2O$, is a white, crystalline powder, mol wt 826.87, sp gr 4.6, lead oxide content 79.8% PbO, moisture loss (2 h at 105°C), 0.3%; sieve analysis, 99.9% through 44 µm (325 mesh); water solubility, nil. In PVC, it provides excellent heat stability; excellent processibility, allowing high extrusion rates; excellent electrical properties over a wide range of temperatures and insulation classifications; good compatibility and low reactivity with a broad range of plasticizers; and for vinyl foams, it is an effective activator for azodicarbonamide-type blowing agents. Other applications include flexible extruded and molded PVC compounds, where it provides good resistance to early color development during processing. In vinyl plastisols, it provides low viscosity build-up on aging.

For vinyl compounds, the general range of dibasic lead phthalate stabilizer usage is between 4 and 4 phr resin. In 105° C electrical insulation PVC stocks, approximately 7 phr is required. For vinyl plastics and foams, between 3 and 5 phr of lead stabilizer is recommended.

Coated. Dibasic lead phthalate, coated, is a fluffy white powder, sp gr 3.5-3.9, lead oxide content 72-75% PbO, moisture loss 0.3-0.4%, fineness 99.5-99.9% through 44 µm (325 mesh) (wet), water solubility, nil. In PVC, it offers high resistance to early color development during processing, compatibility with organic ester and polyester-type plasticizers, higher heat stability and electrical properties, higher processing temperatures and production rates, improved retention of physical properties on aging, lower specific gravity, easier dispersion, and extra lubricity with reduced frictional heat development during processing.

Applications of dibasic lead phthalate, coated grade, include 90 and 105° C rated PVC electrical insulation, plastisols, profile extrusions, calendered sheet, and molded products. The recommended range of usage in vinyl electrical insulation is 5–7 parts per hundred resin, depending on the particular insulation classification to be met. In general-purpose extruded and molded PVC stocks, approximately 3–6 phr of coated dibasic lead phthalate is suggested.

15. Lead Silicates

Lead forms acid, basic, and normal, or metasilicates. Commercial lead silicates (frits) are made to specific PbO:SiO₂ ratios for the glass and ceramics industries, the rubber industry as vulcanizing agent, and the plastics industry as a heat and light stabilizer (142). These are supplied as granular or pulverized fusion products. Some physical properties are given in Table 5.

15.1. Lead Monosilicate. Lead monosilicate [10099-76-0] (lead pyrosilicate), 1.5PbO \cdot SiO₂, is a light yellow trigonal crystalline powder, insoluble in water. Its composition, by weight, is 85% PbO and 15% SiO₂. Lead monosilicate is commercially available as granular, <1.68 mm (10 mesh), and ground, 97% through 44 μ m (325 mesh). It provides the most economical method of introducing lead into a ceramic glaze. It is also used as a source of PbO in the glass industry.

15.2. Lead Bisilicate. Lead bisilicate [11120-22-2], PbO \cdot 0.03Al₂O₃ \cdot 1.95SiO₂, is a pale yellow powder, insoluble in water. Its composition, by weight,

is 65% PbO, 1% Al₂O₃, and 34% SiO₂. Lead bisilicate is available as granular, <1.68 mm (10 mesh), and ground, 88% through 44 μ m (325 mesh). It was developed as a low solubility source of lead in glazes, where its high viscosity and low volatility are equally important.

15.3. Tribasic Lead Silicate. Tribasic lead silicate [12397-06-7], $3PbO \cdot SiO_2$, is a reddish yellow powder, sparingly soluble in water. Its composition by weight is 92% PbO and 8% SiO₂. Tribasic lead silicate is available as granular, <1.68 mm (10 mesh), and ground, 99% through 44 μ m (325 mesh). It is used primarily by glass and frit manufacturers and has the lowest viscosity of the three commercial lead silicates. Commercial lead silicates are generally prepared by melting lead monoxide and silica in the desired ratio.

16. Lead Borate

Lead borate monohydrate [14720-53-7] (lead metaborate), $Pb(BO_2)_2 \cdot H_2O$, mol wt 310.82, $d = 5.6g/cm^3$ (anhydrous) is a white crystalline powder. The metaborate loses water of crystallization at 160°C and melts at 500°C. It is insoluble in water and alkalies, but readily soluble in nitric and hot acetic acid. Lead metaborate may be produced by a fusion of boric acid with lead carbonate or litharge. It also may be formed as a precipitate when a concentrated solution of lead nitrate is mixed with an excess of borax. The oxides of lead and boron are miscible and form clear lead-borate glasses in the range of 21 to 73 mol% PbO.

The main use of lead metaborate is in glazes on pottery, porcelain, and chinaware, as well as in enamels for cast iron. Other applications include as radiation-shielding plastics, as a gelatinous thermal insulator containing asbestos fibers for neutron shielding, and as an additive to improve the properties of semiconducting materials used in thermistors (143).

17. Lead Titanate

Lead titanate [12060-00-3] (lead metatitanate), PbTiO₃, mol wt 302.09, d = 7.52g/cm³, forms yellow tetragonal crystals below 490°C and cubic crystals above 490°C. It is insoluble in water. In hydrochloric acid, lead titanate decomposes into PbCl₂ and TiO₂. It can be formed by calcining an equimolecular mixture of lead monoxide and titanium dioxide and has been used in surface coatings as a pigment in outdoor paints (144), as a component of ceramic electrical insulators (145), in ceramic ferroelectric-piezoelectric compositions (146), in ceramic glazes (148), in transducers (147) (see CERAMICS AS ELECTRICAL MATERIALS), in ceramic glazes (148), in transducers (149), in low melting glass sealants (150), and in oxidation catalysts for manufacturing acrylonitrile from propylene and nitrous oxide (151).

18. Lead Zirconate

Lead zirconate [12060-01-4], $PbZrO_3$, mol wt 346.41, has two colorless crystal structures: a cubic perovskite form above 230°C (Curie point) and a

pseudotetragonal or orthorhombic form below 230°C. It is insoluble in water and aqueous alkalies, but soluble in strong mineral acids. Lead zirconate is usually prepared by heating together the oxides of lead and zirconium in the proper proportion. It readily forms solid solutions with other compounds with the ABO_3 structure, such as barium zirconate or lead titanate. Mixed lead titanate-zirconates have particularly high piezoelectric properties. They are used in high power acoustic-radiating transducers, hydrophones, and specialty instruments (152).

Other salts include lead arsenates and lead arsenites (see Insect control technology), lead chromates and lead silicochromates, lead cyanide (see Cyanides), lead 2-ethylhexanoate (see Driers and metallic soaps), and lead fluoroborate.

19. Health and Safety Factors

Lead is poisonous in all forms, but to different degrees, depending on the chemical nature and solubility of the lead compound. Exposure may be acute or chronic. Because the symptoms of lead poisoning may be similar to those of other ailments, they should be checked with blood and urine tests. Lead is one of the most hazardous toxic metals because the poison is cumulative, and its toxic effects are many and severe. Prolonged absorption of lead or its inorganic compounds can cause the onset of lead poisoning symptoms or plumbism, including weakness, lassitude, weight loss, insomnia, hypotension, and anemia. Associated with these may be gastrointestinal disturbances. Physical signs are usually facial pallor, malnutrition, abdominal tenderness, and pallor of the eye grounds. On gingival tissues, a line or band of blue-black pigmentation (lead line) may appear, but only in the presence of poor dental hygiene.

The alimentary symptoms may be overshadowed by neuromuscular dysfunction, accompanied by signs of motor weakness that may progress to paralysis of the exterior muscles or the wrist (wrist drop), and less often, of the ankles (footdrop). Encephalopathy, the most serious result of lead poisoning, frequently occurs in children as a result of pica, ie, ingestion of inorganic lead compounds in paint chips; this rarely occurs in adults. Nephropathy has also been associated with chronic lead poisoning (153). The toxic effects of lead may be most pronounced on the developing fetus. Consequently, women must be particularly cautious of lead exposure (154). The U.S. Center for Disease Control recommends a blood level of less than 10 μ m per 100 mL for children.

Lead is absorbed into the human body after inhalation of the dust or ingestion of lead-containing products. Contamination of smoking materials in the work area leads to inhalation of lead fumes and constitutes a main factor in lead absorption.

The toxicity of the various lead compounds appears to depend upon several factors: (1) the solubility of the compound in the body fluids; (2) the fineness of the particles of the compound (solubility is greater in proportion to the fineness of the particles); (3) conditions under which the compound is being used. Where a lead compound is used as a powder, contamination of the atmosphere will be much less if the powder is kept damp. Of the various lead compounds, the carbonate, the monoxide, and the sulfate are considered to be more toxic than metallic

OSHA regulations (156) limit exposure to inorganic lead compounds of an employee without a respirator to $50 \,\mu\text{g/m}^3$ air as a time-weighted average (TWA) in an eight-hour shift. This standard went into effect on March 1, 1979.

Measurement of airborne lead concentrations may be made with a gravimetric dust-sampling kit. The apparatus draws in air from the breathing zone of a worker at a controlled rate. This air is passed, with contaminants, through a filter, where the particulate matter is trapped. After a specified length of time, the amount of lead on the filter is determined by analysis. If initial air sampling shows exposure for all employees to be below an action level of $30 \ \mu m/m^3$ of air, averaged over an eight-hour period, only rechecking is needed when any change takes place which might affect lead exposure. On the other hand, if initial air sampling is between 30 and 50 $\mu g/m^3$ of air, averaged over an eight-hour period, then testing must be continued every six months.

However, if air sampling establishes that the lead exposure concentration is excessive, engineering controls (such as improved ventilation), administrative controls (such as job rotation), and work practices (such as improved personal hygiene of workers) have to be applied to comply with the permissible exposure limit (PEL) of the OSHA standard.

In addition to limits on airborne lead, an OSHA regulation provides for biological monitoring and places limits on blood lead levels in workers of $50 \ \mu g/100 \ g$ of whole blood.

Physical examinations, employee training and educational programs, medical protection, and record keeping, among others, are required. The regional OSHA office should be consulted for the latest rules and regulations.

In most cases, proper precautions provide worker safety. According to conditions in the workplace, all workers handling inorganic lead compounds should avoid creating dust, avoid inhaling or swallowing dust, wash thoroughly before eating or smoking, and keep inorganic lead compounds away from animal feed and food products. Adequate care and attention paid to safe handling practices can effectively minimize or eliminate any health risks associated with the handling, storage, use, and disposal of lead compounds.

The OSHA limits, regulations, and recommendations apply to in-plant air quality. Improperly filtered exhaust air may cause a plant to be in violation of the EPA standard, therefore these data should not be confused with the EPA limit for airborne lead, $1.5 \,\mu g \, \text{lead/m}^3$, measured over a calendar quarter, which pertains to the exterior plant environment and emissions. The installation and proper maintenance of exhaust filtration systems enables most plants to comply with the EPA limits for airborne lead (see LEAD COMPOUNDS, INDUSTRIAL TOXICOLOGY).

BIBLIOGRAPHY

"Lead Compounds (Inorganic)" in *ECT* 1st ed., Vol. 8, pp. 267–274, by A. P. Thompson, The Eagle-Picher Co.; "Inorganic Compounds" under "Lead Compounds" in *ECT* 2nd ed., Vol. 12, pp. 266–282, by A. P. Thompson, Eagle-Picher Industries, Inc.; "Lead Salts" under "Lead Compounds" in *ECT* 3rd ed., Vol. 14, pp. 160–180, by D. S. Carr, International

Lead Zinc Research Organization, in *ECT* 4th ed., Vol. 15, pp. 132–152, by D. S. Carr, Consultant, and W. C. Spangenberg and K. Chronley, Hammond Lead Products, Inc.; "Lead Compounds" under "Fluorine Compounds, Inorganic" in *ECT* 1st ed., Vol. 6, pp. 709–710, by F. D. Loomis, Pennsylvania Salt Manufacturing Co.; "Lead" under "Fluorine Compounds, Inorganic" in *ECT* 2nd ed., Vol. 9, pp. 626–627 by W. E. White, Ozark-Mahoning Co.; in *ECT* 3rd ed., Vol. 10, pp. 756–757 by D. T. Meshri, Ozark Mahoning Co.; in *ECT* 4th ed., Vol. 11, pp. 379–380, by Dayal T. Meshri, Advance Research Chemicals, Inc.; "Lead Salts" in *ECT* (online), posting date: December 4, 2000, by Dodd S. Carr, Consultant, William C. Spangenberg, Hammond Lead Products, Inc., Kevin Chronley, Hammond Lead Products, Inc.; "Fluorine Compounds, Inorganic, Lead" in *ECT* (online), posting date: December 4, 2000, by Dayal T. Meshri, Advance Research Chemicals, Inc.

CITED PUBLICATIONS

- 1. S. Afr. Pat. 68 04,061 (Dec. 18, 1968), J. Prior and A. Florin (to Dynamit Nobel A.-G.).
- Ger. Offen. 1,903,879 (Oct. 30, 1969), S. Cane and L. E. Cooper (to BP Chemicals (U.K.) Ltd.).
- 3. Ger. Offen. 1,421,872 (Feb. 19, 1970), W. Reichelt and H. Eligehausen (to W. C. Heraeus GmbH).
- 4. Rus. Pat. 69 18,745 (Aug. 15, 1969), M. Mikoda and T. Hikino (to Matsushita Electric Industrial Co., Ltd.).
- 5. Ger. Offen. 2,106,118 (Sept. 2, 1971), F. Auzel.
- 6. Jpn. Kokai 74 27,442 (Mar. 11, 1974), K. Morimoto and M. Kuroda (to Matsushita Electric Industrial Co., Ltd.).
- 7. U.S. Pat. 3,745,044 (July 10, 1973), E. C. Letter (to Bausch and Lomb, Inc.).
- 8. Jpn. Kokai 74 14,996 (Feb. 8, 1974), N. Ichinose and Y. Yokomizo (to Tokyo Shibaura Electric Co., Ltd.).
- 9. D. T. Meshri and W. E. White, *George H. Cady ACS Symposium*, Milwaukee, Wis., June 1970.
- 10. A. L. Henne and T. H. Newby, J. Am. Chem. Soc. 70, 130 (1948).
- 11. A. L. Henne and T. P. Waalkes, J. Am. Chem. Soc. 67, 1639 (1945).
- 12. A. Bowers and co-workers, J. Am. Chem. Soc. 84, 1050 (1962).
- 13. Ger. Pat. 1,167,828 (Apr. 16, 1964), K. Bruckner and H. J. Mannhardt (to E. Merck AG).
- 14. D. Greninger, V. Kollonitsch, and C. H. Kline, *Lead Chemicals*, International Lead Zinc Research Organization, Inc., New York, 1975, p. 173.
- 15. Brit. Pat. 1,235,100 (June 9, 1971), (to Toyota Central Research and Development Laboratories, Inc.).
- 16. Fr. Pat. 1,556,127 (Jan. 31, 1969), (to Imperial Chemical Industries, Inc.).
- 17. Brit. Pat. 1,078, 854 (Aug. 9, 1967), (to Mitsui Petrochemical Industries, Ltd.).
- U.S. Pat. 3,468,710 (Sept. 23, 1969), D. Krasnov and J. Goodman (to Nuclear Research Associates, Inc.).
- U.S. Pat. 3,484,312 (Dec. 16, 1969), F. Ermanis and B. Schwartz (to Bell Laboratories).
- 20. U.S. Pat. 3,475,372 (Oct. 28, 1969), C. L. Gable (to Mobay Chemical Co.).
- U.S. Pat. 3,468,843 (Sept. 23, 1969), W. F. Busse (to E. I. du Pont de Nemours & Co., Inc.).
- Ger. Offen. 2,051,925 (May 6, 1971), J. Tanaka and M. Watanabe (to Senju Metal Industry Co., Ltd.).

- 23. U.S. Pat. 3,495,944 (Feb. 17, 1970), J. J. McGee, T. J. Kelly, and J. N. Harman (to Beckman Instruments).
- 24. U.S. Pat. 3,562,944 (Feb. 9, 1971), M. A. DeAngelo and D. J. Sharp (to Western Electric Co.).
- 25. U.S. Pat. 3,360,337 (Dec. 26, 1967), M. I. Edenbaum and M. I. Hampton (to Johnson & Johnson).
- 26. U.S. Pat. 3,346,383 (Oct. 10, 1967), R. W. Baxendale (to Eastman Kodak Co.).
- 27. Ger. Offen. 1,956,513 (June 18, 1970), W. A. Van den Heuvel and co-workers (Agfa-Gevaert A.G.).
- 28. Ger. Offen. 1,956,713 (June 18, 1970), J. E. Vanhalst, E. M. Brinckman, and W. A. Van den Heuvel (to Agfa-Gavaert A.G.).
- Fr. Pat. 2,039,700 (Jan. 15, 1971), J. A. Peterson and H. W. Marciniak (to Hooker Chemical Corp.).
- 30. U.S. Pat. 3,287,540 (Nov. 22, 1966), T. J. Connelly (to Allied Chemical Corp.).
- 31. Ref. 14, p. 183.
- 32. U.S. Pat. 3,377,169 (Apr. 9, 1968), R. K. Blake (to E. I. du Pont de Nemours & Co., Inc.).
- 33. Czech. Pat. 121,444 (Jan. 15, 1967), L. Kacetl, J. Pantoflicek, L. Sramek, and F. Anyz.
- 34. Brit. Pat. 1,235,100 (June 9, 1971), (to Toyota Central Research and Development Laboratories, Inc.).
- 35. U.S. Pat. 3,511,715 (May 12, 1970), J. C. Angus (to Valley Co., Inc.).
- 36. F. R. Pat. 1,467,694 (Jan. 27, 1967), (to N. V. Philips Gloeilampenfabrieken).
- 37. USSR Pat. 457,121 (Jan. 15, 1975), S. G. Ashurkov, G. S. Sarychev, and E. F. Fufaev.
- 38. U.S. Pat. 3,467,555 (Sept. 16, 1969), C. M. Henderson, E. R. Beaver, and L. J. Reitsma (to Montana Research Corp.).
- 39. U.S. Pat. 3,460,996 (Aug. 12, 1969), I. Kudman (to Radio Corporation of America).
- 40. U.S. Pat. 3,201,347 (Aug. 17, 1965), J. J. Chessick and J. B. Christian (to U.S. Dept. of the Air Force).
- 41. U.S. Pat. 3,713,996 (Jan. 30, 1973), E. C. Letter (to Bausch and Lomb, Inc.).
- J. J. Wijnbergen, W. H. Moolenaar, and G. DeGroot, Astrophys. Space Sci. Libr. 30, 243 (1972).
- 43. G. Smoluk, Mod. Plast. 56(9), 74 (1979).
- 44. G. R. Smith, Mineral Commodity Summaries, U.S. Geological Survey, Jan. 2004.
- 45. Ref. 14, p. 52.
- 46. Ref. 14, 59-60.
- 47. Ref. 14, p. 69.
- 48. Jpn. Kokai 73 28,396 (Apr. 13, 1973), E. Torikai, Y. Kawami, and Y. Maeda.
- 49. Ger. Offen. 2,156,414 (July 13, 1972), Y. Kuniyasu, T. Sakai, and T. Ogami (to Mitsui Mining and Smelting Co., Ltd.).
- 50. Ger. Offen. 2,142,001 (Apr. 6, 1972), T. Sakai, S. Kobayashi, K. Miyazaki, and M. Yamamoto (to Mitsui Mining and Smelting Co., Ltd.).
- 51. Fr. Pat. 1,511,984 (Feb. 2, 1968), (to Teijin Ltd.).
- 52. Ger. Offen. 2,124,145 (Dec. 30, 1971), A. A. Shul'zhenko and F. Get'man (to Ukrainian Scientific Research Institute of Instruments and Extrahard Materials).
- 53. U.S. Pat. 3,847,861 (Nov. 12, 1974), T. Largman and H. Stone (to Allied Chemical Corp.).
- 54. Ger. Offen. 2,053,706 (May 10, 1972), S. Roth and R. Willig (to Siemens A.G.).
- 55. Jpn. Kokai 76 20,248 (Feb. 18, 1976), H. Kato (to Dainichi-Nippon Cables, Ltd.).
- 56. "Lead", Minerals Yearbook, U.S. Geological Survey, Reston, Va., 2002.
- 57. B. Anderson and G. Eckwall, FATIPEC Congr. 8, 45 (1966).
- 58. L. V. Nitsberg, L. A. Bobina, and O. Y. Khenven, Zashch. Korroz. Gidrotekh. Sooruzhenii Rechn. Vodakh, 182 (1968).

- 59. Jpn. Kokai 74 27,525 (Mar. 12, 1974), A. Minoshi, H. Tsugukuni, and Y. Chikazoe (to Dai Nippon Toryo Co., Ltd.).
- 60. Austrian Pat. 324,922 (Sept. 25, 1975), (to R. Avenarius Chemische Fabrik).
- 61. Jpn. Kokai 74 61,269 (June 13, 1974), I. Ogasawara and S. Kawashima (to Unitika Ltd.).
- 62. USSR Pat. 400,932 (Oct. 1, 1973), V. V. Novoderezhkin and co-workers.
- 63. Jpn. Kokai 73 56,712 (Aug. 9, 1973), T. Yamada and M. Tachibana (to Nippon Sheet Glass Co., Ltd.).
- 64. Jpn. Kokai 76 39,742 (Apr. 2, 1976), K. Ohtsuki and K. Eguchi (to Dainippon Printing Co., Ltd.).
- 65. Ger. Offen. 2,034,053 (July 15, 1971), S. Kobayashi, K. Miyazaki, and M. Yamamoto (to Mitsui Mining and Smelting Co., Ltd.).
- 66. Rus. Pat. 69 10,115 (May 12, 1969), Y. Ishitani and S. Akimaru (to Asahi Chemical Industry Co., Ltd.).
- 67. USSR Pat. 224,022 (Aug. 6, 1968), V. V. Vargin and co-workers.
- 68. Rus. Pat. 71 03,473 (Jan. 28, 1971), K. Minakawa (to Japan Electric Co., Ltd.).
- 69. Ger. Offen. 2,063,586 (July 22, 1971), M. Hamasaki, I. Kurokawa, and N. Izawa (to Asahi Chemical Industry Co., Ltd.).
- 70. Jpn. Kokai 74 46,586 (May 4, 1974), T. Shiki, K. Kozaki, and T. Harada (to Asahi Chemical Industry Co., Ltd.).
- D. M. M. Ibrahim and G. M. Gad, Sprechsaal Keram. Glas Email Silik. 103, 768 (1970).
- 72. Ger. Offen. 1,954,887 (May 6, 1970), J. T. Oetzel (to B. F. Goodrich Co.).
- U.S. Pat. 3,907,585 (Sept. 23, 1975), J. Francel and J. E. King (to Owens-Illinois, Inc.).
- 74. Jpn. Kokai 72 15,414 (Aug. 22, 1972), O. Sato.
- 75. J. W. Diggle and A. Damjanovic, J. Electrochem. Soc. 119, 1649 (1972).
- 76. Jpn. Kokai 74 01,719 (Jan. 9, 1974), K. Suszuki, A. Kanayama, and T. Shimomura (to Tanabe Seiyaku Co., Ltd.; Nitto Electric Industrial Co., Ltd.).
- 77. Brit. Pat. 1,281,527 (July 12, 1972), W. G. Wink.
- 78. Jpn. Kokai 75 16,045 (Feb. 20, 1975), Y. Morioka (to Sanyo Electric Co., Ltd.).
- 79. Rus. Pat. 74 29,164 (Aug. 1, 1974), S. Ono, K. Nakamura, and Y. Mizoguchi (to Asahi Chemical Industry Co., Ltd.).
- USSR Pat. 333,238 (Mar. 21, 1972), B. G. Milov, S. K. Kitaeva, and M. A. Chagina (to Central Scientific-Research Institute of Paper).
- 81. U.S. Pat. 3,766,984 (Oct. 23, 1973), K. H. Nimerick (to Dow Chemical Co.).
- Ger. Offen. 2,128,845 (Feb. 17, 1972), H. E. Meissner and S. D. Stookey (to Corning Glass Works).
- 83. U.S. Pat. 3,791,520 (Feb. 12, 1974), G. J. Nieuwenhuls.
- 84. Ger. Offen. 1,913,099 (July 2, 1970), G. Tanaka and M. Shono (to Giken Kogyo K.K.).
- 85. Ger. (GDR) Appl. 21,328 (Aug. 4, 1958), E. Boeck and G. Keil.
- 86. U.S. Pat. 3,260,613 (July 12, 1966), E. C. Otto (to Interchemical Corp.).
- 87. N. Ogata and H. Kakihana, Nippon Genshiryoku Gakkaishi 11(2), 82 (1969).
- 88. Ref. 14, pp. 140–141.
- 89. Ref. 14, p. 153.
- D. Baresel, W. Sarholz, P. Scharner, and J. Schmitz, Ber. Bunsenges. Phys. Chem. 78, 608 (1974).
- 91. U.S. Pat. 3,877,988 (Apr. 15, 1975), A. N. Dey and P. Bro (to P. R. Mallory and Co., Inc.).
- 92. S. Afr. Pat. 73 07,956 (Nov. 8, 1972), N. Habler and H. Schreiner (to Siemens A.-G.).
- 93. Ger. Offen. 2,210,525 (Nov. 2, 1972), K. Higashiyama and H. Hirata (to Matsushita Electric Industrial Co., Ltd.).

- 94. F. A. Blum and K. W. Nill, Proceedings International Conference, Laser Spectroscopy (AD-777 751), 1974, 449–509.
- 95. U.S. Pat. 3,851,291 (Nov. 26, 1974), A. Sommer (to Ceramic Magnets, Inc.).
- 96. Ref. 14, p. 69.
- 97. Ref. 14, p. 256.
- 98. Fr. Pat. 1,425,881 (Jan. 21, 1966), (to English Clays Lovering Pochin & Co., Ltd.).
- 99. D. N. Gritsan, D. S. Shun, and L. N. Serpukhova, Zh. Prikl. Khim. 34, 1528 (1961).
- 100. Brit. Pat. 827,646 (Feb. 10, 1960), P. H. Haycock, J. J. Ryan, and M. Tuson (to Tootal Broadhurst Lee Co., Ltd.).
- 101. Brit. Pat. 812,785 (Apr. 29, 1959), J. d'Ans, H. E. Freund, and H. J. Schuster.
- 102. Ref. 14, p. 235.
- 103. Brit. Pat. 1,004,309 (Sept. 15, 1965), (to Kurashiki Rayon Co., Ltd.).
- 104. U.S. Pat. 3,238,047 (Mar. 1, 1966), R. D. Murray and E. Berman (to Itek Corp.).
- 105. Rus. Pat. 61 13,944 (Feb. 24, 1959), T. Isojima and H. Terada (to Mitsubishi Rayon Co., Ltd.).
- 106. I. Puhac, N. Hrgovic, M. Stankovic, and S. Popovic, Acta Vet. (Belgrade) 13, 3 (1963).
- 107. Rus. Pat. 63 16,627 (Sept. 2, 1963), Y. Nakahara (to New Japan Electric Co., Ltd.).
- 108. C. Drotschmann, Batterien 17, 569 (1964).
- 109. U.S. Pat. 3,033,675 (May 8, 1962), N. Hedley (to American Cyanamid Co.).
- 110. Ref. 14, p. 201.
- 111. Neth. Appl. 69 02,804 (Aug. 29, 1969), (N. V. Phillips' Gloeilampenfabrieken).
- 112. U.S. Pat. 3,298,833 (Jan. 17, 1967), J. Gaynor (to General Electric Co.).
- 113. Ref. 14, p. 296.
- 114. Fr. Pat. 1,356,569 (Mar. 27, 1964), R. E. Hatton and L. R. Stark (to Monsanto Co.).
- 115. Neth. Appl. 64 08,827 (Feb. 2, 1965), (to Wallace and Tiernan, Inc.).
- 116. S. Kobayashi and S. Hayakawa, Jpn. J. Appl. Phys. 4(3), 181 (1965).
- 117. Rus. Pat. 18,963 (Sept. 4, 1964), S. Futami (to Teijin Ltd.).
- 118. Fr. Pat. 1,404,162 (June 25, 1965), (to Plekhanov Mining Institute).
- 119. U.S. Pat. 3,112,772 (Dec. 3, 1963), R. E. Connor and J. C. Kitching (to H. K. Porter Co., Inc.).
- 120. Neth. Appl. 65 11,631 (Mar. 9, 1966), (to Shell Internationale Research Maatschappij N.V.).
- 121. Neth. Appl. 65 04,192 (Oct. 4, 1965), (to Dow Corning Corp.).
- 122. Belg. Pat. 639,509 (May 4, 1964), (to Farbwerke Hoechst A.-G.).
- 123. U.S. Pat. 3,253,912 (May 31, 1966), J. L. Rooney and J. P. Badger (to Electric Auto-Lite Co.).
- 124. Brit. Pat. 982,564 (Feb. 10, 1965), J. G. Jarvis (to Kodak Ltd.).
- 125. U.S. Pat. 3,260,613 (July 12, 1966), E. C. Otto (to Interchemical Corp.).
- 126. Rus. Pat. 63 03,910 (Apr. 20, 1963), F. Kato and Y. Machino.
- 127. Fr. Addn. (Nov. 3, 1961), to Fr. Pat. 1,165,582 (to Compagnie Generale de Telegraphic Sans Fil).
- 128. Neth. Appl. 64 08,291 (Jan. 21, 1966), (to Mining Institute, Leningrad).
- 129. Ref. 14, p. 216.
- 130. Rus. Pat. 64 20,533 (Sept. 19, 1964), K. Nuruchina, Y. Takehisa, and J. Ichikawa (to Toyo Rayon Co., Ltd.).
- 131. U.S. Pat. 3,039,989 (June 19, 1962), W. O. Eastman (to General Electric Co.).
- 132. U.S. Pat. 2,950,981 (Aug. 30, 1960), H. A. Miller and L. M. Greenstein (to Francis Earle Labs, Inc.).
- 133. Fr. Pat. 1,335,076 (Aug. 16, 1963), (to Tempil Corp.).
- 134. U.S. Pat. 3,231,645 (Jan. 25, 1966), R. A. Balomey (to Mearl Corp.).
- 135. U.S. Pat. 3,138,547 (June 23, 1964), B. L. Clark (to 3M Corp.).

- 136. Neth. Appl. 65 09,144 (Jan. 18, 1966), (to Shell Internationale Research Maatschappij N.V.).
- 137. K. K. Chowdhry, LABDEV (Kanpur, India) 3, 219 (1965).
- 138. U.S. Pat. 3,116,190 (Dec. 31, 1963), F. A. Zihlman, C. N. Bernstein, and F. C. Thames (to the U.S. Navy).
- 139. B. Levi and I. Mekjavic, Tehnika (Belgrade) 16, 1461 (1961).
- 140. Brit. Pat. 917,082 (Jan. 30, 1963), (to National Lead Co.).
- 141. Norw. Pat. 105,779 (Jan. 9, 1965), T. Ringvold.
- 142. Ref. 14, pp. 230–231.
- 143. Ref. 14, p. 210.
- 144. Ref. 14, p. 94.
- 145. USSR Pat. 262,201 (Jan. 26, 1970), O. S. Didkovskaya, V. V. Klimov, and Y. N. Venevtsev.
- 146. U.S. Pat. 3,463,732 (Aug. 26, 1969), H. Banno and T. Tsunooka (to NGK Spark Plug Co., Ltd.).
- 147. Fr. Pat. 1,533,488 (July 19, 1968), S. A. Long and C. L. Fillmore (to Globe-Union Inc.).
- 148. U.S. Pat. 3,405,002 (Oct. 8, 1968), F. W. Martin (to Corning Glass Works).
- 149. U.S. Pat. 3,517,093 (June 23, 1970), J. J. Wentzel (to U.S. Dept. of the Navy).
- 150. Jpn. Kokai 76 13,820 (July 25, 1974), I. Matsuura and F. Yamaguchi (to Nippon Electric Glass Co., Ltd.).
- 151. V. M. Belousov and co-workers, Katal. Katal. (10), 37 (1973).
- 152. Ref. 14, p. 96.
- 153. M. H. Proctor and J. P. Hughes, *Chemical Hazards of the Workplace*, J. B. Lippincott Co., Philadelphia, Pa., 1978, p. 308.
- 154. P. B. Beeson and W. McDermott, *Textbook of Medicine*, W. B. Saunders Co., Philadelphia, Pa., 1975, Vol. 1, p. 58.
- 155. R. J. Lewis, Sr., Sax's Dangerous Properties of Industrial Materials, 10th ed., John Wiley & Sons, Inc., New York, 2000.
- 156. Code of Federal Regulations, Title 29, Part 1910.1025, OSHA, Washington, D.C., 1979.

GENERAL REFERENCES

- D. Greninger, V. Kollonitsch, and C. H. Kline, *Lead Chemicals*, International Lead Zinc Research Organization, Inc., New York, 1975.
- J. W. Mellor, Inorganic and Theoretical Chemistry, Vol. III, Longmans, Green & Co., New York, 1930, 636–888.
- A. T. Wells, Structural Inorganic Chemistry, 3rd ed., Clarendon Press, Oxford, U.K., 1962, particularly pp. 475–479, 902–903.

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Property	$PbBr_2$	$PbCl_2$	PbF_2	PbF_4	PbI_2
CAS registry number	[10031-22-8]	[7758-95-4]	[7783-46-2]	[7783-46-2]	[10101-63-0]
mol wt mp, °C	$376.04 \\ 373$	$278.1 \\ 501$	$245.21 \\ 855$	$\begin{array}{c} 283.2\\ 600 \end{array}$	$\begin{array}{c} 461.05\\ 402 \end{array}$
bp, °C	916	950	1290	decomposes	954
d, g/cm ³ soly, g in 100 mL H ₂ O	6.66	5.85	8.24	6.7	6.16
at 0°C 20°C	0.455	$0.673 \\ 0.99$	0.064	a	$\begin{array}{c} 0.044 \\ 0.063 \end{array}$
$100^{\circ}\mathrm{C}$	4.71	3.34			0.41

Table 1. Physical Properties of Lead Halides

a Material hydrolyzes to PbO₂ and HF.

Property	PbO	PbO_2	Pb_2O_3	Pb_3O_4
CAS registry number	[1317-36-8]	[1309-60-0]	[1314-27-8]	[1314-41-6]
mol wt	223.21	239.21	462.42	685.63
mp, °C	897^a			830^b
dec, °C	1472^c	290	370	500
$d, g/cm^3$				
α	9.53	9.375		9.1
β	9.6			
crystal structure				
α	tetragonal	orthorhombic (columbite)		spinel^d
β	orthorhombic	rutile		

Table 2. Physical Properties of Lead Oxides

^aBegins to sublime before melting. ^bWhen decomposition is prevented by oxygen pressure.

^c Boiling point. ^d Unit cell contains four Pb_3O_4 groups.

Property	$PbSO_4$	$PbO \cdot PbSO_4$
CAS registry number mol wt mp, °C $d, g/cm^3$	$[7446-14-2] \\ 303.25 \\ 1170^a \\ 6.2$	$[12765-51-4] \\ 526.44 \\ 977 \\ 6.92$
$\begin{array}{c} \mathrm{soly,g/100\ mL\ H_2O}\\ \mathrm{at\ 25^{\circ}C}\\ \mathrm{40^{\circ}C} \end{array}$	$4.25 imes 10^{-3}\ 5.6 imes 10^{-3}$	$4.4 imes10^{-3b}$
crystal structure	orthorhombic, monoclinic	monoclinic

Table 3. Physical Properties of Lead Sulfates

^{*a*} Decomposes above 900°C. ^{*b*} At 0°C.

LEAD COMPOUNDS 25

Table 4. Physical Properties of Lead Acetates

Property	Anhydrous	Basic	Trihydrate	Tetraacetate
${f mol wt} {f mp, \ ^{\circ}C} {f d, g/cm^3} {f refractive index, n_{ m D}} {f soly, g/100 mL H_2O}$	$325.28 \\ 280 \\ 3.25$	807.69 75 (200 dec)	379.33 75 (200 dec) 2.55 1.567^a	$\begin{array}{c} 443.77 \\ 175 \\ 2.228 \end{array}$
at 15°C 100°C	$\frac{44.3^b}{221^c}$	$\begin{array}{c} 6.25\\ 25\end{array}$	$\begin{array}{c} 45.61 \\ 200 \end{array}$	

^{*a*} Along the β-axis. ^{*b*} At 20°C. ^{*c*} At 50°C.

Property	Monosilicate	Bisilicate	Tribasic silicate
$rac{mol wt}{mp, °C}$ $d, g/cm^3$ refractive index, n_p	$\begin{array}{c} 294.85 \\ 700-784 \\ 6.50-6.65 \\ 2.00-2.02 \end{array}$	343.37 788-816 4.60-4.65 1.72-1.74	729.63705-7337.522.20-2.24

Table 5. Physical Properties of Lead Silicates