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LEAD INDUSTRIES ASSOCIATION, INC.
292 MADISON AVENUE
NEW YORK, N. Y. 10017

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SUBJECT: REPRINT ON LEAD IN GLASS

To the Members of the Lead Industries Association, Inc.:

The enclosed reprint, entitled "Importance of Lead in Glass" has just been received from The Glass Industry magazine, where it recently appeared.

This comprehensive report and bibliography was compiled under an International Lead Zinc Research Organization grant at the State University of New York, College of Ceramics, at Alfred.

We will distribute this reprint to students of glass technology at all universities offering such a course, and in addition it will be offered to selected technical reference libraries and to persons involved in the investigation and manufacture of lead-bearing glasses.

You may obtain up to 10 copies of this report, free of charge, and additional copies may be had at our cost of 35¢ per copy.

Very truly yours,

Jerome F. Smith

JFS:so'h

Jerome F. Smith

Look Ahead with Lead

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Importance of Lead in Glass

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Importance of Lead in Glass

By Craig F. Leiser

Mr. Leiser, now supervisor of new product development, reactor materials, for Minnesota Mining and Manufacturing Co., assembled this bibliography under a Fellowship of the International Lead Zinc Research Organization in association with the Lead Industries Association while at the State University of New York College of Ceramics at Alfred. Additional references were collected by Mr. and Mrs. Jean Blachere under a continuation of the Fellowship. Further search and revision of the report were due to Miss Megan Greene. Professor Charles H. Greene, Chairman of the Department of Glass Technology at Alfred, directed the work and edited the final text.

Part One

Lead oxide has been used as a major constituent in glass since the very beginning of glassmaking. Although the early glasses of Egypt generally contained little, if any, lead, Chinese glass dating back to the sixth century B.C. usually contained major quantities, and glass objects from Mesopotamia around the same period had large proportions of lead oxide. E. R. Caley[1] has recently published an excellent summary of our knowledge of ancient glass compositions which shows the widespread use of lead oxide in early glass manufacture.

The materials in primitive glass manufacture were impure so that the glass was strongly colored. The early lead glasses often contained copper, which resulted in red tints when melting conditions were reducing, and blues when the glasses were oxidized.

It is very probable that early glass manufacture derived from the art of glazing ceramic ware, in which lead compounds were widely used. Thus, analyses of glazes found on pots in Tarsus show that Roman craftsmen knew of this use of lead oxide[2,3]. Parmelee[4] comments on the widespread and continuous use of lead in glazes. The strong fluxing action of lead oxide allows the formulation of glazes which mature at a relatively low temperature just as its use in glass compositions facilitates melting and produces soft glasses which can be shaped at low temperatures.

However, the use of lead oxide in glass to achieve clarity and brilliance was virtually unknown until 1675 when Ravenscroft invented English crystal. Before that date, the ultimate in fine glassware was the Venetian "cristalo" produced from a soda-lime-silica composition. The flourishing English and Irish lead crystal industries which grew up rapidly after Ravenscroft's discovery, were evidence of the fading of Venetian and Italian supremacy. The secret spread quickly all over Europe, reaching Russia in less than fifty years. Since the eighteenth century, lead oxide has been used routinely as a constituent of the finest crystal glass.

A variety of new applications for lead glasses were discovered during the last century. Lead oxide is indispensable in optical, solder, electrical, and radiation absorbing glass. The special properties of lead glasses which make them useful for so many purposes are:

1. Wide working range at a relatively low temperature.
2. High index of refraction
3. High dispersion
4. Resistance to devitrification
5. Low electrical conductivity
6. Strong absorption of X-rays and gamma rays.

The great fluxing power of lead oxide makes it invaluable in fusible compositions for bonding other materials and formulating colored enamels and glazes.

The following references provide additional background on the history of the use of lead[5,6,7,8,9,10] in glass and glazes.

Composition

The practical empirical experience of glassmakers demonstrates that lead oxide is compatible with all oxide glass forming systems. Among metallic oxides which do not form glasses by themselves when pure, lead oxide is unique in that a very large proportion of it may be combined with minor proportions of typical glass-forming oxides to yield stable glasses. Thus, melts containing over 90 per cent by weight of lead oxide with silica and boric oxide may be cooled to glasses. Lead oxide also combines with oxides of other heavy elements, which do not themselves form glasses, to yield unusual glass compositions. Systems of PbO with TeO, V_2O_5, and Sb_2O_3 are said to form glasses, although it appears that the addition of small quantities of silica to such compositions facilitates cooling without crystallization. As has been demonstrated by Sun,[9] lead fluoride also may be combined with other fluorides to form glasses of unusual compositions and properties. These facts show that lead compounds, although not by themselves glass formers, are particularly adaptable to glass compositions. Hence, study of the desirable properties which lead contributes to glass is most important to the scientist concerned with

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2. E. R. Caley, "Results of a Chemical Examination of Some Specimens of Roman Glass from Tarsus," Amer. J. [illegible]
3. Anonymous, "Report on Roman Pottery Glazes," Ceram. Age 52 (1948) 78.
4. C. W. Parmelee, "Ceramic Glazes," 2nd Ed. [illegible] Industrial Publications [illegible]
5. K. [illegible] "Lead Glass [illegible]" [illegible]
6. C. G. Seligman, "Far Eastern Glass: Some Western Origins," Bull. Mus. Far Eastern Antiquities No. 10 [illegible]
7. W. E. S. Turner, "The Analyses of Ancient Glasses," Glass Ind. 36 [illegible]
8. Morey, "Properties of Glass" (New York: Reinhold Publishing Corp., 1954).
9. K. H. Sun, "Fluoride Optical Glasses," U. S. Pats. [illegible]

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the application of glass to wide varieties of special uses and with development of new glasses for particularly difficult applications.

The early scientific investigations by Schott and his co-workers in Jena between 1880 and 1900 covered many lead glasses. The results of this work are available in Hovestadt's book on Jena Glass[10] where the properties of the glasses are correlated with their compositions.

An even more extensive study of the relation between the composition of glass and its properties was carried out in the early 1920's by Peddle[11]. Six series of lead glasses were melted, each series with a different ratio of alkali to silica. The lead oxide content of the glasses in each series was increased in a regular fashion. In two of the series soda was the only alkali; in two others, potash was used alone while in the remaining two an equimolecular mixture of soda and potash was used. Study of similar glasses containing lime and other divalent oxides permitted a comparison of these with lead oxide.

G. W. Morey[8] summarizes the work of Peddle and many other investigators upon lead containing glasses, while M. B. Volf[12] provides a convenient source of data on the physical and chemical properties of lead glasses.

The practical limits of the composition fields for lead-containing glasses are determined by various properties of these glasses. In the direction of high silica, the limit is set by difficulty in melting; too high alkali content leads to glasses which are so unstable chemically that they are attacked by atmospheric moisture; very high lead oxide content may cause difficulty from crystallization. In the 1920's various authors published generalized formulas purporting to describe the useful fields of lead glass compositions[13,14,15,16]. These formulas were the subject of much controversy, however, and have not proven very useful in the formulation of commercial glasses.

A much better basis for compounding high lead glasses is provided by phase rule work on simple ternary systems containing lead oxide and silica. The work of Geller and Bunting on the K_2O-PbO-SiO_2 system[17] is most illuminating, while work by Krakau, Mekhin, and Heinrich on the Na_2O-PbO-SiO_2 system[18] is equally useful. Phase rule diagrams alone give no information on the glass forming potentialities of a system, but observations on crystallization velocity made during the experimental study of such a system provide a rich source of glass making information. Liquidus temperatures are valuable to the glass technologist, since they indicate the thermal ranges which must be avoided in the practical manufacture of glass.

Besides the practical technological limits on the compositions of lead glasses, legal restrictions also exist. Since lead oxide is relatively expensive, manufacturers tend to use as little as possible in their batches[19]. However, since the brilliance, sonority and value of real crystal depend on its lead content, the governments in many countries have imposed minimum requirements for the lead oxide content of ware labeled "crystal." Thus "Bohemian lead crystal" was required to contain at least 20 per cent of lead oxide[20]. The German product, permitted to bear the label "lead crystal" on a gold seal, contains no less than 18 per cent lead oxide[21], while the French designate only glass with at least 24 per cent lead oxide as "crystal"[22].

It should be noted that rather small quantities of lead oxide are sufficient in some cases to impart desirable properties to glass compositions. Approximately five per cent lead oxide in a hard borosilicate formula is sufficient to facilitate the melting of the batch and to improve the electrical surface resistance of the glass greatly[8 (p. 479)].

Much further information on lead glass compositions will be found in the later sections of this report concerned with the manufacture, properties, and specific applications of lead glasses.

Structure

Modern ideas on the structure of glass begin with a paper by W. H. Zachariasen[24] in which rules deduced from the known structures of crystalline silicates were applied to glass. Studies of the diffraction of X-rays by glass made by B. E. Warren and his associates[25] supported this theory by showing that the essential unit in the structure of silicate glasses is a regular tetrahedron composed of four oxygen atoms surrounding a central silicon atom. Warren's X-ray results also showed that beyond this first neighbor distance the ordering of atoms in glass rapidly becomes entirely random and that any regions of regular crystalline pattern existing in glass are extremely small. G. J. Bair[26] applied the X-ray diffraction technique to lead glasses and showed that Zachariasen's ideas explain the arrangement of constituent atoms observed in them also. Bair concluded that the structure of PbO-SiO_2 glass consists of an interlocking network of atoms in which lead atoms are always separated by silicon-oxygen tetrahedra and never occur adjacent to each other or joined to each other by a common oxygen.

According to the Zachariasen-Warren picture, glass is built up of Oxygen ions and two kinds of metal ions. One kind of metal ion (e.g. Si^{4+}) links the oxygens together to form a random network of tetrahedra. The other kind of metal ion (e.g. Na^{+}) fills the holes in this network and modifies its properties.

Many metallic consituents of glass, however, cannot be classified uniquely in either of these groups but act at times as network formers and at other times as network modifiers. Lead ions play this dual role in glass. At low concentrations lead acts as a network modifier, but at high concentrations it must form part of the network. In a glass with the composition of lead

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10. Hovestadt, "Jena Glass and Its Scientific and Industrial Applications," MacMillan Co. (1902).
11. C. J. Peddle, "The Development of Various Types of Glasses," Parts VI-IX, J. Soc. Glass Technol., 4 (1920), 299-366; Part X, 5 (1921), 72; Part XI, 5 (1921), 195-201; Part XVI, [illegible] (1921), 256.
12. M. B. Volf, "Technical Glasses" (London: Sir Isaac Pitman & Sons, Ltd., 1961), "Sealing Glasses," 270-[illegible].
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14. O. Knapp, "Keppeler's Rule for Lead Glasses," Sprechsaal 58 (1925), 110; J. Soc. Glass Technol. 9 (1925), 113.
15. F. Zschimmer, "On the Theory of the Composition of Glass," J. Soc. Glass Technol. 14 (1930), 129.
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17. R. F. Geller and E. N. Bunting, "The System K_2O-PbO-SiO_2," J. Res. Nat. Bur. Standards 17 (1936), 277.
18. K. A. Krakau, E. J. Mekhin and M. N. Heinrich, "Equilibrium Diagram of the Ternary System Na_2SiO_3-$PbSiO_3$-SiO_2," C. R. Acad. Sci., URSS, 16 (1937), 281; Trans. Brit. Ceram. Soc. 37 (1938), 266A.
19. [illegible] Sprague, "What is Crystal Glass," Glastech. Ber. 19 (1933), 253-270.
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21. Anonymous, "The R.A.L. Marking Regulations for Lead Crystal Glass," Glastech. Ber. 11 (1933), 271.
22. Anonymous, "The Standardization of Crystal," Courier de Normalisation [illegible] (July-August 1940), 921.
23. W. Zachariasen, "The Atomic Arrangement of Glass," J. Am. Chem. Soc. (1932), 3841.
24. B. E. Warren and J. Biscoe, "Fourier Analysis of X-ray Patterns of Soda-Silica Glass," J. Am. Ceram. Soc. 21 (1938), 259-65; J. Appl. Phys. 11 (1942), 602.
25. G. J. Bair, "The Constitution of Lead Oxide-Silica Glasses," Part I and II, J. Am. Ceram. Soc. 19 (1936), 339, 347.

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orthosilicate, Pb_2SiO_4, the SiO_4 tetrahedra must be joined by lead ions.

Many authors have discussed this ability of lead ions to form part of the network structure of glass. Moore and Carey[26] decided that lead either forms double span linkages (≡Si-O-Pb-O-Pb-Si≡) or enters the glass structure as a tetrahedral group (PbO_4). These conclusions contradict Bair's interpretation of his X-ray results. Stanworth[27] suggested that lead acts as a network former by forming essentially covalent bonds with neighboring oxygens while retaining a low coordination number. Weyl[28] explains the behavior of lead in glass by his screening theory. The polarizable Pb^{++} ion behaves on one side as a highly charged tetravalent ion while the other side shows the character of a noble metal. This theory proves useful in explaining the surface properties of lead glasses.

Jones and Kreidl[29] as well as Fajans and Kreidl[30] have also discussed the asymmetric behavior of lead ions in glass and have linked this with the optical properties of lead glasses. Papers by Callow[31], Florinskaya[32], and Jenckel[33] treat the structure of lead glasses. Callow concludes from phase rule and volatilization data that lead silicate tends to segregate from silica-rich regions in glasses of the binary SiO_2-PbO system.

Manufacture

Lead glass is melted in closed pots, open pots, and continuous tanks. It is preferred for "off hand" blowing in artistic ware because of its long working range, but also lends itself to all types of automatic fabrication. Much lead glass is made into tubing by Danner and Vello machines and used for sealing leads in incandescent lamps and electronic tubes. Lead glass tubing is also preferred for making neon signs because it is so soft and readily shaped. Continuous tanks are built of fusion cast refractories for satisfactory production of lead glass.

Optical glass, which must be of the highest quality, requires stirring to obtain satisfactory homogeneity. This may be done in open pots with a refractory rod. Platinum crucibles and continuous melting units lined with platinum are provided with efficient platinum stirrers. Great care must be taken when lead glass is melted in platinum to avoid reduction of the lead oxide in the glass, since metallic lead produced in this way alloys with platinum and ruins it. Electric heating is advisable to avoid this danger[34,35,36,37,38,39,40].

Litharge, or lead monoxide, is the primary material used for introducting lead into glass batches. For crystal and optical glasses where freedom from color is essential, high purity of the litharge and other raw materials is necessary. Because iron is a common and particularly undesirable impurity, it is essential to use litharge which is free from iron and other coloring oxides. Fortunately, this requirement has been met by the lead industry–lead oxide with less than 50ppm of iron may be purchased for use in fine glasses. A process for making pure litharge by oxidizing a spray of molten lead is described by S. R. Scholes[41].

Since lead glasses are subject to reduction, it is often desirable to supply extra oxygen in the batch. One way is to use red lead, Pb_3O_4, which is obtained by roasting litharge, PbO, in a current of air. It gives up its extra oxygen early in the melting process and helps to oxidize chance organic impurities in the batch[42,43,44].

The physical form of litharge is a matter of concern to the glassmaker. Various steps may be taken to avoid difficulty from dusting and waste due to its finely divided form. Binders may be added to convert litharge into a granular material which can be handled by mixing and filling equipment without objectionable dust[45]. The influence of moisture on the mixing of potash-lead-silica glass was studied by Turner and co-workers[46,47]. According to this work, about 4 per cent is the optimum amount of water to be added to such batches.

Another way of avoiding dusting of lead oxide from glass batches is to convert it to lead silicate by a preliminary fusion with silica. Goldschmidt[48] describes a method for doing this in an open hearth furnace. The lead silicate obtained by this process is itself a glass and may be used for adding lead oxide to glass batches in a completely non-dusting free-flowing form. It has the further advantage of reducing the melting time of the glass and diminishing cords[49,50,51].

These dustless materials also have the advantage of facilitating proper hygiene in mixing and handling glass batch. Trouble may be entirely avoided with lead oxide, arsenious oxide, and similar glass material, by proper supervision to ensure adequate hygienic precautions–wearing dust masks, through bathing, and periodic medical tests. Even quartz sand, for example, must be handled with care to avoid silicosis, and therefore similar precautions must be taken in mixing a glass batch[52].

In lead glass batches cullet has a

26. H. Moore and M. Carey, "Limiting Compositions of Binary Glasses of the Type [illegible] and the Ternary Type [illegible] and [illegible] in Relation to Glass Structure," Trans. Soc. Glass Technol. 35 (1951), 68.
27. J. Stanworth, "On the Structure of Glass," J. Soc. Glass Technol. 32 (1948), 154.
28. W. A. Weyl, "Glass Composition," Ceram. Age 50 (1947), 34.
29. H. L. Jones and N. J. Kreidl, "Thermal Properties and the Constitution of Glass," J. Soc. Glass Technol. 31 (1947), 290.
30. K. Fajans and N. J. Kreidl, "Stability of Lead Glasses and Polarization of Ions," J. Am. Ceram. Soc. 31 (1948), 105.
31. R. J. Callow, "Relations in the System $PbO-SiO_2$," Trans. Faraday Soc. 47 (1951), 370.
32. V. A. Florinskaya, "Transmission Spectra of Thin Silicate Glass Films in the Infrared," Chem. Abstr. 46 [illegible]; Doklady Akad. Nauk SSSR 86 (1952), [illegible].
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37. Anonymous, "Modern Straight Line Production Featured in New Corning Factory," Am. Glass Rev. 49 (1930), 14.
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43. R. Hoecke, "Metallic Lead in Red Lead," Glastech. Ber. 11 (1928), 366; J. Soc. Glass Technol. 11 (1927), 614.
44. R. Schmidt, "The Requirements of a Pure Red Lead for Glass Making and the Method of Testing," Keram. Rundschau 30 (1922), [illegible]; J. Soc. Glass Technol. 12 (1928), [illegible].
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47. M. Parkin and W. E. S. Turner, "The Influence of Moisture on the Mixing of Batches for Potash-Lead Oxide-Silica Glass," J. Soc. Glass Technol. 10 (1926), 213T.
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49. Anonymous, "Lead Sand Reduces Melting Time," Ceram. Ind. 31, (1938), 98.
50. L. Scheidl, "Process of Manufacturing Lead Glass," U. S. Pat. [illegible], (Sept. 9, 1952).
51. A. N. Smith, "Theoretical Relationship Between the Solubility of Lead in Silicate Frits and Their Specific Surface," Trans. Brit. Ceram. Soc. 50 (1951), 257.
52. C. Stone, "Laws and Regulations Relating to Lead Poisoning," (London: Imperial Mineral Resources Bureau, 254 pp., 1922).

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beneficial action in the melting process and diminishes the corrosive action of the batch materials on the pots. English, Hodkin, and Turner[53] published a description of the effects of cullet in varying proportions on potash-lead-oxide-silica glasses. Rees[54] pointed out a difficulty arising from the use of scraps of tubing as cullet in a lead glass: the tubing trapped raw materials, causing chemical inhomogeneity in the glass and producing cords. It was recommended that the cullet be crushed to small pieces to avoid this difficulty.

Although lead oxide or lead silicate is usually employed in making up batches for lead glass, other materials have been proposed at times. Thus, Beyersdorfer[55] proposed the use of metallic lead with an oxidizing agent and Harkort[56] patented the use of storage battery waste. Hirsch[57] reported that use of lead sulfide ores as a source of lead in glass batches is not to be recommended. Lead sand[49] is recommended to diminish melting time.

Various non-lead materials have been proposed as a substitute for lead oxide in glass batches. This, of course, is a matter of glass composition, and the extent to which such substitutions can be tolerated depends on the use to which the glass is to be put. Barium oxide[58], lime with silica and alumina[59], sodium pyrophosphate and borax[60], and various other replacements for PbO have been proposed. In general, such replacements may be practical to a limited extent, but some sacrifice of the desirable properties imparted to glass by lead oxide is involved.

A major problem in all glass melting is corrosion of the containing refractories. Although lead glass is no more active in this respect than soda-lime glass, the high density of lead-containing glass and the volatility of lead oxide from lead glass may introduce special problems. Thus, Preston and Turner[61] noted that corrosion of the inside of the crown and the pot mouth in closed pots melting potash-lead-silica glasses is caused by lead oxide volatilized during melting. Porous refractory in the bottom of a lead glass pot is rapidly penetrated by the dense glass. Hence, it is advisable to use a plastic clay which fires to a dense vitreous body even though this increases the care which must be taken to avoid cracking during drying and firing of lead glass pots. Such pots are dissolved more evenly and more slowly than pots of more porous material and cause fewer stones and cords in the glass[50,62]. Firth[63] recommends firing pots to the melting temperature of the glass, or above, to minimize corrosion. The longer the time such pots are under fire, the more resistant they become to glass attack.

Volatilization of lead oxide from lead glass melts introduces other problems as well as those of refractory attack during the melting operation. Inhomogeneity caused by loss of lead from the surface glass may cause cordiness. If this is avoided by sufficient mixing, the overall glass composition may be changed so as to materially affect its physical properties.

Anderson[64], who was one of the first to study the evaporation of lead oxide from lead glass melts, found that the rate of volatilization depends to a large extent on the amount of stirring to which the glass is subjected. At temperatures between 900° and 1400°C the rate of evaporation from an unstirred pot falls off rapidly after the first 15 minutes. This is due to the formation of a thin layer of glass low in lead and, consequently, of low density which floats on the surface of the melt. Consequently, the rate of loss of lead from an unstirred melt depends on the rate of diffusion of lead to the surface rather than on the rate of evaporation. Anderson's results indicated that a ton of dense flint glass containing 60 per cent PbO may lose as much as 25lb. of lead oxide when melted for 2 days in a 39 in. pot. This is sufficient to change the lead content of the glass by about 1.2 per cent and to diminish the refractive index by 5 units in the third decimal place. It is obvious from these results that the time and temperature must be carefully controlled during the melting of lead glasses if serious variations in the optical properties of the glass are to be avoided.

Hallse and Cook[65] pointed out that alumina is an important factor in the volatilization of lead because of its great influence on the viscosity of glass. Hirayama[66] reported that the evaporation of lead from borate glasses is less than from silicates of corresponding lead content.

Preston and Turner[67,68], were led by observations of the attack of lead vapors on glass pots to make a detailed study of the evaporation of lead oxide from lead glass melts. They also determined the actual vapor pressure of lead oxide over molten lead glass by a dynamic method in which a stream of inert gas was saturated by passing over the glass. As would be expected, the initial rate of volatilization from the glass melts changed in the same way with temperature as the equilibrium vapor pressure. The rate of lead oxide volatilization at a constant temperature of 1200°C increased as the percentage of lead in the glass increased and the curve connecting lead volatilization with glass composition showed breaks at points corresponding to the compounds $PbSiO_3$ and Pb_2SiO_4. Preston and Turner interpreted this as evidence for the existence of these compounds in the glass, supposing that each compound had its own characteristic evaporation rate.

R. J. Callow[51] used the results of Preston and Turner to estimate the activities of both PbO and SiO_2 in the binary system. Although calculations using Kelley's data[69] on heats of

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51. R. J. Callow, "Activities in the System $PbO-SiO_2$," *Trans. Faraday Soc.* 47 (1951), 370.
52. Anonymous, "The Melting of Lead Glass in Open Pots," *J. Soc. Glass Technol.* 1 (1917), 878.
53. S. English, G. A. Green, F. Hodkin and W. E. S. Turner, "The Effect of Cullet on the Melting and Working Properties of Potash-Lead Oxide-Silica Glasses," *J. Soc. Glass Technol.* 11 (1927), 7.
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68. F. Preston and W. E. S. Turner, "Volatilization of Lead Oxide from Lead Oxide-Silica Mixtures," *J. Soc. Glass Technol.* 19 (1935), 296-311.
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formation with the freezing points from phase rule work indicate positive deviations from ideal behavior at high concentrations of PbO in SiO_2, calculations from the vapor pressure work with the phase rule data show nearly ideal behavior up 15 per cent of SiO_2 followed by increasing negative deviations in the activity of PbO at higher silica concentrations. The activity of silica follows an "S"-shaped curve with large positive deviations from ideal solution behavior at high concentrations of silica.

Callow[73] interprets these curves as evidence that lead ions when added to silica glass tend to order the oxygen ions about themselves and to segregate from regions containing comparatively undifferentiated silica. This tendency is not sufficient to cause separation into two glassy phases—as it is in the systems containing calcium, strontium, and barium ions—but it is similar, and more marked than the deviations in the alkali-silica systems. As more PbO is added, the formation of orthosilicate groups eventually leads to strong negative deviations from ideal behavior for the activity of SiO_2. These calculations are particularly interesting for the light they throw on the structure of lead silica glasses.

The reactions occurring during the melting of potash-lead-silicate glasses have been studied by Preston and Turner[70] in England, by Besborodov et al[71] in Russia, and by Tamman and Oelsen in Germany[72] with similar results. Moisture is evolved and oxygen is liberated from Pb_3O_4 below 600°C. Potassium carbonate reacts with silica between 600° and 800°C, while PbO reacts with SiO_2 and K_2O above 700°C. At 1000°C the PbO has entirely dissolved in the melt, and above 1000°C final solution of residual silica takes place and is completed at 1200°C. Details of the reactions in this complex system vary with the rate of heating and with grain size of the batch.

The reaction between lead oxide and silica, which constitutes a simpler subsystem of the potash-lead-glass melting reaction, has been studied by an even larger group of investigators[72,74,75,76,77,78,79]. As a result of the work it is generally agreed that three compounds are formed in this system, lead metasilicate, $PbSiO_3$, melting at 764° 30C.; lead orthosilicate, Pb_2SiO_4, melting at 743° 30C.; and a basic silicate, Pb_4SiO_6, melting at 725° 1°C. Lead oxide, PbO, melting at 886° 2°C., is the primary phase for mixtures containing less than 6.7 weight per cent of SiO_2, and silica crystallizes from mixtures containing more than 29.5 per cent of SiO_2.

Preston and Turner[70] studied the rate of glass formation in the reaction between red lead (Pb_3O_4) and quartz sand (SiO_2), as well as the mechanism of the reaction. They found the first step in this reaction to be decomposition of the Pb_3O_4 with release of oxygen, leaving PbO. This step was completed at about 500°C. Above this temperature PbO was transferred in the vapor phase to the surface of the silica grains. Here it reacted to form a lead-rich glass which gradually penetrated and dissolved the grains. X-ray diffraction studies showed that the final product of the reaction did not contain free silica and that there was no solid solution of lead oxide in quartz lattice in the course of the reaction. The rate of the reaction increased as the temperature increased as shown in Table I for a mixture containing 80 per cent of lead oxide. All of these studies are useful in providing scientific background for the practical melting of high lead glasses.

Surface tension is a property of glass which has a great influence on its behavior in melting. Jebsen-Marwedel[80] has pointed out its importance in the mechanisms by which refractories are corroded and cords formed or dispersed in glass. When soft lead-containing glasses are used as bases for enamels and glazes, surface tension is again most important in determining spreading and wetting behavior[81]. In general, lead glasses rank low in surface tension, with values in the range from 210 to 230 dynes/cm. at 1,000°C. According to the work of Shartsis and others, glasses containing large amounts of lead oxide have positive temperature coefficients of surface tension[82,83].

TABLE I—Rate of glass formation between PbO and SiO_2

Temperature (°C)	Time for a Clear Melt
1000°	31 min.
1100	18 "
1200	14 "
1300	8 "
1375°	4 "

Sulfur oxides in the batch and tank atmosphere also influence the surface of lead glass melts. Study of the lead sicilate-lead sulfate system by Merker and Wondratschek[84] revealed that these glasses possess very low surface tensions.

Partridge[85] traced the cause of a precipitate in melts of a 30 per cent lead crystal glass to the presence of sulfur dioxide in the furnace gases. Beyersdorfer[86] also found that sulfur dioxide, which is always present in producer gas, will cause the precipitation of lead sulfate if the concentration of oxygen in the atmosphere over the glass is sufficient to cause the oxidation of SO_2 to SO_3. Thus, although it is essential to melt lead glasses in an oxidizing atmosphere, the oxygen content should not be more than one per cent during cooling of the glass.

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Badger[87] found that incorporation of about 3 per cent of lead oxide in glass-making refractories results in an increase in resistance to corrosion. Also, the cords, which result from solution of such lead-containing refractories, have lower surface tension than the main body of glass and are more easily homogenized than cords from ordinary refractories.

Lead glasses are generally characterized by low annealing temperatures. Thus, Gehlhoff and Thomas[88] in comparing PbO with CaO, BaO, and other divalent oxides substituted for silica in a base glass containing 18 per cent Na_2O and 82 per cent of SiO_2, found it to be the most effective of the oxides tried in lowering the temperature at which strain disappeared quickly when the glasses were heated[88 (p. 166-168)] at 5° per min. Lillie[89], defining the annealing point as the temperature at which glass has a viscosity of 10^{13} poises, found values ranging from 419° to 451°C for Corning lead glasses, while the annealing points of lime glasses were about 50°C higher, and those of borosilicates about 100°C higher.

In any glass melting operation tests to ensure that the composition and properties of the product are kept constant are important. This is particularly necessary with lead glasses because of the loss of lead oxide by volatilization during melting. Probably the most frequently used determination for this sort of quality control is the measurement of density. Experiments by Manners and Partridge[90] demonstrated the effectiveness of refractive index measurements as a control of the quality of lead glass for tubing manufacture. L. Dubrul[91] recommends measurement of two properties such as density and softening point for more reliable control of glass composition.

In the manufacture of lead glass the analysis of glass and raw materials for lead is important. Allen and Zies[92] describe methods of determining lead and barium, while Sandell[93] and Schmid[94] discuss the determination of lead in silicates. Tests for iron and other impurities in lead raw materials are necessary[95]. Tests for small quantities of lead extracted from glass, enamels, and glazes are also needed. Included here are references on some of the numerous methods which have been published[96,97,98,99,100,101,102,103,104].

Properties

Some of the properties of lead glasses such as volatility, surface tension, and viscosity which are of importance in the manufacturing process have already been discussed. Others are of special importance for the products in which lead glasses are used and will now be treated.

Durability

Chemical durability is one of the most essential qualities of glass. Lead glasses in general show good resistance to attack by water but are less resistant to acid and alkaline solutions. As has been explained in the section on structure, Weyl[105] attributes the stability of lead glass surfaces toward attack by water to the asymmetric nature of the lead ion. This permits it to direct its bonding force toward the interior of a piece of glass while to the surface it presents the aspect of a noble metal atom. This also explains the non-hygroscopic nature of lead glass and its low surface conductivity. A. Boettcher[106] noted the advantage of lead glass in vacuum systems due to its small absorption of water, and H. Simpson found it superior to other glasses in a cyclic dimming test[107].

Knapp[108], Peddle[11], Morey and Bowen[109], Dimbleby and Turner[110], and Cauwood, Webb, and Turner[111] have all investigated the resistance of lead glass compositions to attack by aqueous solutions. In general, solubility increases with alkali content. Potash-lead glasses are more durable than soda-lead glasses containing the same weight percentage of alkali, but there is a marked maximum in the durability when soda is replaced by potash at the composition where the ration of potash to soda is two to one. Moderate amounts of lead oxide are effective in stabilizing glass against attack by acid and alkaline solutions, but lead oxide is less efficient in this respect than lime and some other divalent oxides. In the dense flint glasses, which contain 50 per cent or more of lead oxide, stability toward acids becomes poor.

Apostolian and Kreidl[112] found that TiO_2, ZrO_2, Nb_2O_5, and Ta_2O_5 were all effective in improving the durability of a 65 per cent SiO_2, 35 per cent PbO glass in acid. TiO_2 was the most effective single oxide in this respect, but a mixture of ZrO_2 and TiO_2 was better than any single addition. Durability or stain resistance was evaluated by determining the length of time necessary in 1 per cent HNO_3 to form a surface film one-quarter wave-length thick. Vasicek[113] studied the chemical action of dilute sulfuric acid on lead glasses and concluded that the surface film remaining after durability tests of lead glasses is amorphous silica.

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Importance of Lead in Glass

By Craig F. Leiser

Part Two

Mechanical Properties

H. Akmoran[114] *found* that regular increase in the lead oxide content from 10 to 35 per cent resulted in a decrease in Young's modulus according to the equation

$$E = [16100 - 216 \times (\%\ PbO)]$$

psi. Measurements by Spinner[115], Guilbot[116], Krutthoff[117] and Thiele[118] also indicate that increasing amounts of lead oxide decrease the elastic moduli of glass, although variation of other constituents also has a marked effect in some compositions.

Mechanical strength is so closely associated with the surface condition of glass that it is very difficult to obtain any reliable information on the relationship between strength and chemical composition. Tooley and coworkers[119, 120] studied the effect on mechanical strength of soaking various glasses in water. They found that lead glasses did not show as great an increase in strength as a result of the soaking as did the soda-lime and borosilicate specimens. This probably reflects the better resistance of these glasses to solution by water.

Hardness is a property of glass and other substances which is measured in several different ways and which varies according to the method of measurement. In general, lead oxide appears to diminish the hardness of glass, although Ainsworth[121] measuring the diamond pyramid hardness of Na_2O SiO_2 glasses to which increasing amounts of PbO were added found that initial additions caused an increase in hardness which passed through a maximum for the glass containing 15 per cent of PbO. When lead oxide was compared with other divalent oxides added in 10 per cent amounts to the 1:4 soda-silica base, the lead glass was the softest of the group.

When hardness is assessed by resistance to grinding, lead glasses again prove to be soft. Scholes[122] compared different glasses by grinding the ends of rods on a steel plate using quartz sand as an abrasive. Silica and boric oxide contributed resistance to abrasion, while increasing soda, lime, and particularly lead oxide produced soft, easily abraded glasses. Willot[123] obtained similar results, although his table of hardness factors (Table II) ranks lead oxide above soda, potash, and lime.

TABLE II—Hardness factors[123]

SiO_2	10.0	Na_2O	3.7
B_2O_3	6.1	CaO	4.3
PbO	0.9	BaO	0.[illegible]
K_2O	10.2		

Thermal Properties

The specific heat of glass is of interest in calculating the efficiency of melting equipment and because of light which it throws on the structure of glass. Sharp and Ginther[124] have reviewed the literature and assigned constants which may be used for calculating the mean specific heat of glasses. Lead, as might be expected from its large atomic weight, has a small factor relative to lighter elements. Lead glasses also show unusual behavior in the way specific heat varies with temperature. Hartman and Brand[125] have supplied more recent data, which indicates that a 30 per cent lead glass has a low specific heat although not as low as would be calculated with the factors of Sharp and Ginther. Thermal conductivity, a property of importance in the technical applications of glass, is low for lead glass. It may be calculated by an additive formula devised by Sharp and given by Morey[8, p. 290].

Thermal expansion is one of the most important properties of glass in technical use since it determines the strain existing in seals between glass and other materials — also between two glasses and it is a most important factor in the resistance of glass articles to heat shock. Thermal expansion is often predicted for known glass compositions by an *additive formula*: the percentage by weight of each oxide in the glass is multiplied by an appropriate factor such that the sum of these products is equal to the thermal expansion. Several lists of factors have been proposed[9] which are in general agreement but differ in details. Each set of factors works best for glasses in the range of compositions for which it was developed. In general, lead has a factor of intermediate value being neither as high as the alkali metal oxide, nor as low as silica. Senin[126] has given this problem particular attention.

A large amount of work has been published on the development of lead glasses with particular values of thermal expansion[127, 128, 129]. Hidnert[130] has measured the thermal ex-

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pansions of some optical glasses, and Mori[131] of soda-lead glasses. Appen[132] made a particular study of the effect of alkali in lead-silicate glasses on thermal expansion.

The work of Karkanavala[133] illuminates the relationship between thermal expansion and structure in glass. He studied the effect of cation field strength and cation polarizability upon thermal expansion. The lead ion Pb^{2+} is an example of a highly polarizable ion, while Sr^{2+} is a noble gas type of cation of the same charge and similar size. In high-silica glasses these ions do not differ appreciably in their effects on the thermal expansion between 0 and 300°C. However, in low silica glasses there is a difference. The factor for lead increases with decreasing silica content, while that for strontium and barium remains constant.

Optical Properties

Lead oxide is one of the most important constituents in determining the properties of optical glasses. Its effect in increasing refractive index and dispersion is well known. In lead crystal compositions, these optical properties are said to contribute brilliance and sparkle, but here the changes are not accurately controlled.

The early work of Wright[2] on the properties of optical glass provides a background of quantitative information in this field. He showed that the changes in index and dispersion produced by increasing the lead oxide in glass are associated with motion of an absorption band in the ultraviolet toward the visible part of the spectrum.

There is a close correlation between the density of a glass and its refractive index and the addition of lead oxide to a glass increases its density as well as its refractive index. Both properties have been investigated by numerous authors[134–145, 148]. Many lead-containing compositions are disclosed in patents on optical glasses[127, 129, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148]. Among the most useful formulas for the calculation of the density and optical properties of glass of general composition including lead glasses, were those worked out by Huggins and Sun[149].

The effect of sulfate on the densities and refractive indices of lead silicate glasses were studied by Merker and Wendratschek[84]. A comparison[150] showed that glasses having equal molecular percentages of TiO_2 and PbO have similar densities and similar refractive indices. Another study — this one on the effect of adding rare earth ions to various glasses[151] — showed that the results were less noticeable in lead glasses than in soda-lime and phosphate glasses.

The densities and refractive indices of all glasses increase as the glasses are subjected to heat treatment during annealing. This change in lead glasses was studied by Kreshe[152]. The effect of electron bombardment on the density of lead and other glasses was studied by Mike Steuerman and Degering[153].

The color of lead glasses is also of great importance to their use for optical purposes, and in crystalware. As long as the composition of the glass has less than 50 per cent lead oxide, the glass will be colorless and will have a very high optical transmittance, provided traces of coloring oxides are not present as impurities. With larger percentages of lead oxide in the dense flint glasses, a yellow color develops, and the overall transmission falls off[154]. This is noticeable also in the very dense glasses used for absorbing X-rays and gamma rays. Florence, Glaze, Haliner, and Ralphstan[155] found that lead silicates have a better transmission in the infrared than alkali silicates, presumably because of smaller water content. Hertz and Stanford[156] found dense lead glasses designed for radiation shielding may have transmissions ranging from 83 to 89 per cent in the visible.

Flomokava[157] investigated the transmission of infrared rays in the 9.5 to 15μ range through thin films of lead silicate glass, as well as the reflection of these wavelengths. These results were interpreted as indicating the presence of "crystallites" in the glasses.

Pepperhoff[158] also studied the infrared reflection spectra of lead silicate glasses and noticed a similarity with the reflection spectra of crystalline lead silicate in the 20μ region. He concluded that the conditions of order in the vitreous system are similar to those in an intercrystalline compound.

The infrared transmissions of lead glasses containing large proportions of other heavy metal oxides were investigated by Heaton and Moore[159] and by Stanworth[160]. These glasses showed water bands, and none of them transmitted beyond 7.5μ. Apparently anions heavier than oxygen must be used to obtain glasses transmitting at longer wavelengths. Stanworth's lead telluride glasses were opaque in the visible with infrared transmission.

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In the ultraviolet, lead glasses have poor transmissions[161,162]. They are also useful for absorbing X-rays and gamma rays, a property which is dependent on their density. But they do not absorb or stop neutrons effectively unless some other element (such as boron or cadmium) with a large absorption cross section for neutrons is present.

In stopping high-energy radiation, glass is usually colored, often to such an extent that it is useless for visual observation. Lead glass protective windows suffer from this difficulty. However, lead glass differs for other higher melting compositions in that the color caused by X-rays is bleached by the same rays that produce the color so that a state of equilibrium may be reached before the color becomes dark enough to make the glass completely useless for visual work[163,164,165,166,167]. Lead glass compositions have been devised for fibers which may be woven into fabrics useful for X-ray protection[168].

When glass is under a mechanical stress, it becomes birefrigent. In most cases, a uniaxial compression causes the glass to behave like a negative uniaxial crystal, the birefringence being proportional to the stress. In very high lead glasses the sign of this effect is reversed. Pockels[169] studied a series of Jena glasses and, after checking his initial results by an experimental melt, decided that a glass containing about 75 per cent lead oxide would show no birefringence under stress with change in the wavelength of the light passing through the glass and found that the *stress optical coefficient* increases numerically from the red toward the violet but that this effect also is reversed at high lead content[170,171].

Glass containing traces of lead fluoresce when exposed to ultraviolet light of short wavelength (254mu). As the lead content increases, the color of *the fluorescence changes from brilliant* blue to green, reaching a maximum intensity when the lead oxide content is 5 per cent. At 60 per cent PbO, the fluorescence has practically vanished [172,173]. Gilard et al.[174] reported that lead glasses melted under reducing conditions emit salmon colors when exposed to ultraviolet light. Other fluorescing elements, such as uranium, are quenched in lead glass because it absorbs the ultraviolet light[172].

The tints produced in glass by various coloring constituents are frequently dependent on the base composition of the glass. Thus, gold and copper compounds produce ruby glass when dissolved in lead glasses. Uranium produces a bright yellow color in high lead compositions[77]. Opaque white glasses may be obtained by adding arsenates or phosphates to lead glass. These are useful for the white strips in thermometers.

Electrical Properties

Probably the most important technical uses of lead glass depend on their favorable electrical properties. Most glasses show a surface conductivity for electricity which increases with increase in humidity and ruins their insulating value. Lead glasses are less subject to the difficulty than soda-lime, and a lead-containing borosilicate is particularly good[49,67?]. Okamoto and Tuzi[175] have studied the absorption of water on a lead borosilicate glass in a vacuum which is closely related to the surface electrical conductivity.

It is also possible to make the surface of lead glass conducting by heating it in hydrogen. This process was studied by Blodgett[176] for a glass containing about 61 per cent of lead oxide. Others have studied the reduction reaction between the surface of lead glass and reducing flames by *microscopic and electrical means*[177,178,179].

The volume conductivity of lead glass is low, compared with other glass compositions having comparable coefficients of thermal expansion. For optimum resistance values it is desirable to use a mixture of two parts of potash to one part of soda, the same ratio which yields optimum chemical durability. Large quantities of a glass (with the 2-to-1 ratio of K_2O and Na_2O) containing about 29 per cent PbO—generally known as G12 in the industry—is manufactured for use in the electric light and radio tube industries. Here, it is used for insulating pinches to seal the lead in wires. Its thermal expansion must be matched to the less expensive soda-lime glass used for the rest of the bulb. Partridge[180] made a study of the effects of substituting BaO and other oxides for PbO in glasses of this type.

Two other electrical properties which are improved in glass by the presence of substantial quantities of lead oxide in glass are the dielectric constant and the power factor. Because glasses have relatively high dielectric constants, and because of their low softening temperature, which permits hermetic sealing, and their moderate coefficient of expansion they are used in the form of thin ribbons for the dielectric in electrical condensers. Armistead[181] describes suitable compositions.

This use in condensers, as well as other applications where the glass is subjected to high frequency alternating fields, is favored by a low power factor since the power factor is a measure of the energy loss in a dielectric subjected to such fields. From this point of view, the ideal glass is pure fused silica since it contains no mobile ions which may be set in motion by alternating fields to absorb energy.

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However, for many uses, fused silica is to difficult to manufacture, and its very low coefficient of thermal expansion makes the fabrication of gas-tight seals very difficult. As network modifying ions are added to the silica network, the conductivity and dielectric loss generally increase. However, the large doubly charged lead ions appear to be relatively immobile in the glass network so that lead glasses generally have low dielectric losses with favorable working and sealing properties. These matters have been studied extensively by Navias and Green[182,183,184,185], by Stevels, and by Ioffe[186].

Miscellaneous Properties

The diffusion of gas through glass is very important in the manufacture of high-vacuum apparatus. Of all gases, at ordinary temperature helium diffuses most rapidly through glasses especially fused silica because of its open structure. The hard borosilicates rank next. As the openings in the network of the glass are filled by ions, the rate of diffusion of helium decreases, so that lead glasses are the most impermeable to helium. Smith and Taylor[187] and Norton[188] have studied the general problem of the diffusion of gases through glass.

The great fluxing power of lead oxide makes it possible to compound very soft glasses useful as solders for joining parts made of harder glasses. Glasses for this purpose must have a viscosity low enough to flow at a temperature where the glasses to be joined are sufficiently rigid to maintain their shape. Their thermal expansions must match those of the glasses to be joined between room temperature and the temperature at which the solder glass itself becomes rigid. The solder glass must also have sufficient chemical durability to withstand both weathering and any solutions to which the joint may be subjected. These requirements may be met by glasses containing a large proportion of lead oxide with smaller percentages of silica and boric oxide as glass formers and alumina to improve stability[189,190,191]. An example of this type of solder glass contains 3 per cent SiO_2, 11 per cent Al_2O_3, 75 per cent PbO, and 11 per cent B_2O_3. At times, cadmium and zinc oxides are also used in solder glass.

The use of lead oxide in glazes for ceramic bodies, in enamels for metals and glasses, and in frits for bonding powdered mica or abrasives is similar to its use in solder glasses. The fact that very soft glasses with moderate thermal expansions can be formulated is invaluable in these applications. This is particularly valuable where colored pigments are to be incorporated in glazes and enamels. The presence of lead oxide makes it possible to mature such glazes at temperatures so low that colors which would be destroyed by higher firing temperatures may be applied without fading or discoloration. Parmalee's treatise is an excellent source of information on these compositions and many references occur in patent files and the ceramic literature[6,192,193,194,195,196].

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Part III (conclusion)

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