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LEAD INDUSTRIES ASSOCIATION, INC.

292 MADISON AVENUE

NEW YORK, N. Y. 10017

TELEPHONE — AREA CODE 212

OR 9-0050

January 20, 1965

SUBJECT: SUPPLEMENT TO CERAMIC DATA BOOK

To Members of the Lead Industries Association, Inc.:

A press release on the latest supplement to LEAD IN THE CERAMIC INDUSTRIES, along with a copy of the supplement, is enclosed. Entitled "Use of Lead in Solder Glasses", this supplement explains the new devitrifying solder glasses and the role lead plays in their development and application.

This supplement has been mailed to the 7,000 persons who now possess a copy of LEAD IN THE CERAMIC INDUSTRIES for insertion in the binder, and single copies will be distributed in response to requests generated by the enclosed release and by publicity in Lead Magazine.

Information used to prepare the supplement was supplied by the Corning Glass Works, or was gathered from patent literature, and the staff written article was reviewed by the Ceramics Technical Committee prior to publication.

We feel that the supplement will be a useful addition to the ceramic data book while at the same time serving as a good promotional piece by keeping the subject of lead before members of the ceramic industry.

Very truly yours,

Jerome F. Smith

Jerome F. Smith

JFS:df

Enclosures

Look Ahead with Lead

LIA23205

NEWS From Lead Industries Association, Inc.

Look Ahead with Lead

292 Madison Avenue
New York, N. Y. 10017 — OR 9-6020

Further Information: Jerome F. Smith

RELEASE:
Immediate (1/20/65)
LIA 144 (12, 16)

SUPPLEMENT OUT ON SOLDER GLASS SEALING

A new 4-page supplement to LEAD IN THE CERAMIC INDUSTRIES, the ceramic data book published by the Lead Industries Association, Inc., has just been released.

Stable and devitrifying solder glasses -- both high and low temperature -- are discussed from the standpoint of composition differences and sealing characteristics. Advantages and limitations, selecting the proper glass, and completion of the seal are also explained. Three tables and two curves give a variety of typical compositions, electrical properties, expansion characteristics and permissible mismatch data.

Intended as a general primer for those wishing to learn more on the subject, this piece supplements an existing section on solder glass and other glasses found in Section Four of LEAD IN THE CERAMIC INDUSTRIES. Both the supplement and the book are available without charge from the Lead Industries Association, Inc., 292 Madison Avenue, New York City 10017.

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TO THE EDITOR: If you wish, you may have additional copies of this supplement, or, if you have not yet received one, you are welcome to a copy of the ceramic data book, LEAD IN THE CERAMIC INDUSTRIES -- just let us know you'd like one.

N 1691.01

USE OF LEAD IN SOLDER GLASSES*

There are at present two general types of solder glass: the thermoplastic or stable type, and the newer thermosetting or devitrifying type. The latter materials are formed as glass and then converted mostly to crystalline (devitrified) ceramics by subsequent heat treatment.

WHY LEAD IS USED

Lead plays an important role in both types of glass. This is because solder glasses containing large amounts of lead oxide have a low softening temperature, good electrical properties, and PbO has a minimum effect on thermal expansion. In addition, lead helps to maintain good durability of the glass system relative to other low temperature glasses, particularly in the area of moisture resistance. Of course, other oxides may be used in place of lead to achieve low temperature glasses, but few offer the same combined balance of desirable properties. For instance, alkalies may be used to soften glasses, but while so doing they tend to raise expansion, lower electrical resistance and undermine durability.

STABLE SOLDER GLASSES

While compositions lie usually in the high lead region of the system PbO-B_2O_3-Al_2O_3-SiO_2 (often with minor amounts of ZnO), stable or thermoplastic solder glasses are also produced from the PbO-ZnO-B_2O_3 system, sometimes with small additions of SiO_2. See Table 4-5. Such glasses have been used for a number of years to join various glass and glass-to-metal assemblies, e.g., cathode ray tubes, sealed beam headlamps, etc. The ability to fill voids (low viscosity) at temperatures as low as 450°C, seal transparency, and the fact that "preforms" (rods, washers, discs, etc.) may be utilized with this type of solder glass assure its continued use for many applications.

DEVITRIFYING SOLDER GLASSES

Typically, the thermosetting or devitrifying solder glasses are from the system PbO-B_2O_3-ZnO-SiO_2, often with Al_2O_3 or CuO additions, or both. Table 4-6 lists the composition of several devitrifying glasses cited in the patent literature covering such developments. Broadly, these glasses may be separated into two classifications: 1. those for low temperature sealing (375 to 500°C) containing 70-80% lead oxide, and, 2. higher temperature glasses (500 to 700°C) containing 5-20% PbO.

375 TO 500°C DEVITRIFYING GLASSES

A minimum of 70% lead oxide is used in these glasses to assure that they will not be too refractory. Roughly 80% PbO is the upper limit because a larger amount would tend to raise the glass expansion coefficient beyond the useful point for sealing materials with an expansion of 105 × 10⁻⁷ per °C or less. ZnO, the other important glass modifier in this group, is usually kept in the 7 to 14% range.* Even though it does not enter the crystalline phase, it serves to adjust the controlled devitrification process. Concentrations of ZnO greater than 14% tend to accelerate devitrification too rapidly in the presence of PbO, while in amounts less than 7%, devitrification occurs too slowly at the programed "setting-up" temperature.

In some cases, however, devitrification may not be extensive, nor is it always desirable that it be complete. Thus, the resultant seal may have a rather large glassy phase or matrix. In the high lead devitrifying solder glasses, the crystal phase is often a lead borate or borosilicate and the matrix or binder is a zinc glass. With less than 7% ZnO, the glassy phase is too soft to produce a strong, thermal resistant seal. Amounts of B_2O_3 greater than 15% tend to make the glass too stable, hindering formation of the crystalline phase. In addition, B_2O_3 is an extremely active flux, and concentrations are kept low so that the sealing glass will not be too corrosive. Silica and alumina are added in amounts of 2 to 3% as inhibitors of devitrification and to improve weather resistance and softening temperatures.

TABLE 4-5
Stable Solder Glasses Using Lead

	I	II	III	IV	V	VI
PbO	80.0	83.0	17.0	75.0	71.1	67-73
B_2O_3	10.0	10.0	20.0	11.0	15.4	11-21
ZnO			40.0		9.5	0.5-11
SiO_2	5.0	4.0	13.0	3.0	2.1	0-6
Al_2O_3	5.0	3.0		11.0		
CuO			10.0		1.9	0.5-10
Approximate Sealing Temp.	400°C	400°C	570°C	440°C	—	—

* The assistance of Dr. Robert Dalton and others at the Corning Glass Works, Corning, New York, in the preparation of this paper is gratefully acknowledged.

TABLE 4-6
Devitrifying Solder Glasses Using Lead

	I	II	III	IV	V	VI	VII
PbO	77.5	77.5	80.0	77.5	76.5	17.0	5.0
B_2O_3	7.5	9.0	6.5	10.0	9.6	14.0	18.0
ZnO	10.0	10.0	10.0	10.0	11.0	50.0	60.0
SiO_2	2.5	2.5	2.5	2.5	2.5	19.0	15.0
CuO							2.0
Al_2O_3	2.5	1.0	1.0		1.0		
Approximate Sealing Temp.	450°C	450°C	420°C	450°C	450°C	700°C	685°C

Minor additions of other modifiers may be and have been added to these glasses (primarily in place of the PbO and ZnO) to change slightly the seal characteristics—adhesion, strength, expansion coefficient, etc.—without greatly affecting sealing temperatures.

500 TO 700°C DEVITRIFYING GLASSES

These glasses are considerably more refractory than the high lead sealing glasses, and characteristically have lower coefficients of expansion, usually less than 50×10^{-7} per °C (0-300°C). Examples VI and VII in Table 4-6 are typical of this type of devitrifying solder glass. High in ZnO (50 to 60%), these glasses often contain 15 to 20% SiO_2 and 5 to 20% PbO, and seal at around 700°C. A small amount of CuO (2-3%) is said to retard devitrification and thereby reduce the difference in thermal expansion between the glassy and devitrified state of the solder glass composition listed in example VII.

Martin and Zimar have set forth the following advantages and limitations for devitrifying solder glasses.

ADVANTAGES

1. Greater rigidity in high temperature applications. For example, in sealing color TV face panels to the envelope, with subsequent exhaust bake at over 400°C.
2. Lower expansion for a given sealing temperature. With stable solder glasses, a lower effective expansion can only be obtained at the sacrifice of increased sealing temperatures.
3. Stress characteristics may be more desirable. In some instances, it is possible to maintain compression stresses from sealing temperature down to room temperature.
4. Lower stresses within the fillet. Due to differential contraction between the sealing glass and bodies being sealed, viscous displacement can occur during cooling cycle. Devitrifying solder glasses are either set up during the cooling cycle or contraction rates in the setting-up region are often much lower, thus fillet stresses are lower.

LIMITATIONS

1. Sufficient flow for good seal formation is sometimes hard to obtain. And increasing the sealing temperature will not help, since this usually brings about faster devitrification.
2. Glass quality control is considerably more critical.
3. Preglazing is not always possible, and where it is, only a narrow range exists for sintering.
4. The seals are always opaque whereas with stable glasses they may be transparent.

SELECTING A SOLDER GLASS

The requirements for a good solder glass are few but difficult to satisfy:

- Softening temperature well below that of articles being joined—and low enough not to affect heat-sensitive components.
- A viscosity of 10^4 to 10^6 poises at sealing temperature.
- Quick setting (steep viscosity-temperature curve).
- An expansion coefficient as close as possible to the theoretically best value (within $\pm 2 \times 10^{-7}$ per °C considered a good match).
- Acceptable durability in service.

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Depending upon the application, other properties, such as a reasonably good electrical resistance, might be necessary. But with high lead glasses, this requirement is usually easily met. The electrical properties of a (lead-alumino-borosilicate) thermoplastic solder glass are given in Table 4-7. Data on a (lead-alkali-silicate) glass—the stem glass most used for lamps and radio tubes—are given for comparison.

TABLE 4-7
Electrical Properties of a Solder Glass

	Thermoplastic Solder Glass	Stem Glass
Log R at 250°C	10.64	10.1
Log R at 350°C	8.66	8.0
Power Factor*	0.0022	0.0012
Dielectric Constant*	15.6	6.7

* Room temperature, 1 mc.

EXPANSION CONSIDERATIONS

Probably the single most important characteristic of a solder glass is its expansion coefficient. This is the average specific elongation per degree Centigrade from 0° to 300°C. It is approximately linear until the strain point is approached and then it swings upward.

This upward swing or "bend" on the expansion curve is of considerable interest in sealing glass applications because it is here that the strain, annealing and setting-up points are found. For a solder glass this bend will, of course, occur at a lower temperature than for the glass or other material to be sealed. Obviously then, a matching solder glass must have a lower expansion coefficient than the material to be sealed in order to have the same contraction from setting-up point to room temperature. How much lower depends on the setting-up point and on the shape of the solder glass curve.

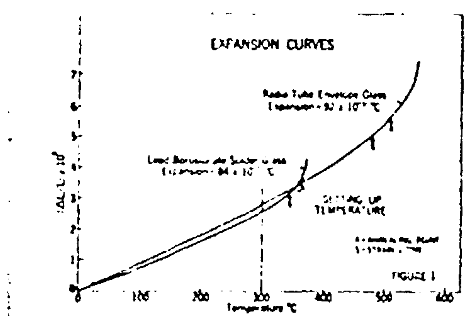
Figure 1 shows a plot of the specific elongation, $\Delta L/L$, versus the temperature for a lead borosilicate solder glass and the soda-lime glass commonly used for radio tube envelopes. These curves are obtained by cooling the glasses at 1°C per minute from a state of equilibrium above the annealing point, and are typical for two glasses which, for most seals, would be considered a good match.

There is no universal answer to the question of how close an expansion match is needed between a solder glass and the article to be sealed. Geometry of the article and the nature of service expected will be determining factors. For an average application, differences of $\pm 2 \times 10^{-7}$ per °C would be considered good, and differences up to $\pm 10 \times 10^{-7}$ per °C are feasible. The permissible departure will increase as one goes to lower temperature (softer) glasses, since the seal then cools through a smaller temperature range after setting up. Figure 2 gives graphic representation of permissible mismatch plotted against setting temperature. It shows clearly that expansion match can only be ignored with very low temperature materials, e.g., sealing wax, etc.

VISCOSITY CONSIDERATIONS

A unique feature of solder glasses is their low temperature fluidity. The fluidity or viscosity necessary to make any given seal depends on the fit between parts, the character of the solder glass, and the time available for the job. With polished surfaces in intimate contact, seals have been made with viscosities as high as 10[illegible] poises—sometimes higher. However, with a poor fit, requiring considerable flow, viscosities may have to be in the range of 10[illegible] poises or lower. The more fluid range, 10[illegible] to 10[illegible] poises is the most useful and generally results in stronger seals.

The amount of deformation that will occur in pieces being joined depends on several factors: 1. geometry of the piece, 2. the external force(s), 3. nature of



Courtesy American Journal of Physics

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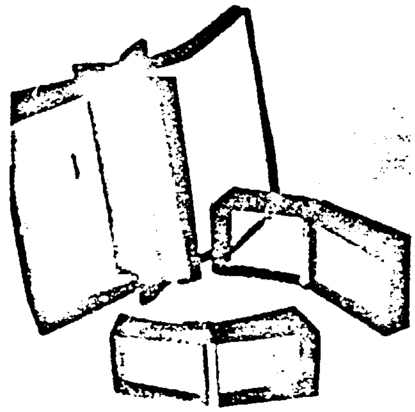
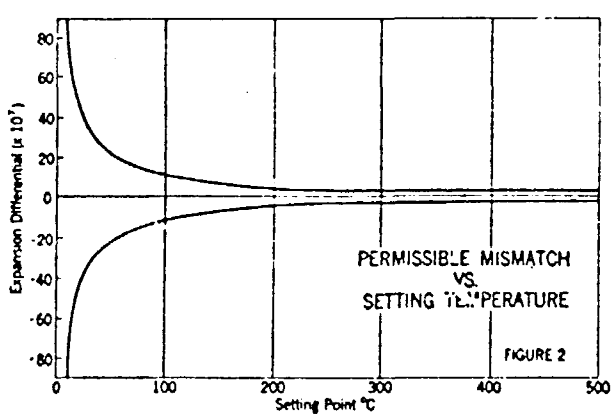
the support, 4. the duration of heating, and 5. solder glass viscosity. As a general guide, where the whole piece is heated, the safe upper limit will be from near the annealing point to perhaps 40°C above. Generally, the working point of the solder glass should be near the annealing point of the article. If local heating is used, higher melting solder glasses can be employed.

1. "Sealing with Solder Glass" by Robert H. Dalton, *American Journal of Physics*, 32, 479 (1964).
2. "Conducting Solder Glass Compositions," U. S. Patent # 3,060,328.
3. "Sealing Glass," U. S. Patent # 3,088,833.
4. "Soft Glass and Composite Article," U. S. Patent # 2,643,020
5. "Glass-to-Glass Seal," U. S. Patent # 2,931,142.
6. "Low-Melting Glass Sealant and Article Made Therefrom," U. S. Patent # 3,127,278.
7. "Devitrifying Solder Glass," U.S. Patent # 2,889,952.
8. "Thermally Devitrifiable Glasses," British Patent # 863,500
9. "Thermally Devitrifiable Sealing Glass," U. S. Patent # 3,088,834; 3,088,835.
10. "Properties and Applications of Devitrifying Solder Glasses" by Francis W. Martin and Frank Zimar, from *The Proceedings of the Sixth Symposium on the Art of Glassblowing* (1961)



Courtesy Corning Glass Works

Samples of joints made with devitrifying solder glasses of the type used in joining all-glass TV tubes. About the same consistency as toothpaste before firing, this material makes strong seals with good electrical resistance.



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