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LEAD INDUSTRIES ASSOCIATION

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NEW YORK 17, N. Y.

March 10, 1958

SUBJECT: SUPPLEMENT TO "LEAD IN THE CERAMIC INDUSTRIES"

To Members of the Lead Industries Association:

Enclosed is the second supplement to our technical data book, "Lead in the Ceramic Industries," issued in December, 1956. This supplement covers "Low-Temperature Glasses as Bonding Materials for Crystals."

This is being mailed to all of the 5,000 people connected with the ceramic industries who have already received the book and will also be included with future copies of the book sent out in answer to requests for it. It will be followed by other supplements from time to time, some of which are already in preparation.

Very truly yours,

Secretary.

March 1958

LOW-TEMPERATURE GLASSES AS BONDING MATERIALS FOR CRYSTALS*

MECHANICAL AND PHYSICAL FUNCTIONS

The principal applications of low-temperature glasses as bonding materials for crystals fall into the following categories.

(a) Glass is used as a supporting medium for crystals—to hold a crystal in place or to make possible a desired configuration or shape for a number of crystals. If temperature and other factors are not important this purpose is served by litharge-glycerin or other cements; but if elevated temperature and low dielectric loss or high surface resistivity are important, then low-temperature glasses are essential.

(b) It is sometimes desirable to disperse crystals with reasonable uniformity throughout a given volume, and to maintain the distribution. Ferroelectric materials, for example, may be dispersed in a number of media, often organic plastics; but low-temperature glasses offer obvious advantages from the viewpoints of thermal characteristics and geometric or dimensional stability over a period of time.

(c) The agglomeration of small crystals into larger masses constitutes an essential commercial application of low-temperature glasses. The most prominent such application is that of agglomerating powdered mica (actually very small crystals) into glass-bonded mica, a ceramoplastic which may be molded and machined. Titanates, ferrites, wollastonite, and a large number of other materials may be so agglomerated.

(d) If crystals are bonded with low-temperature glasses of high lead content, it is possible to increase the density where this is desirable.

(e) Often, when large crystals are sealed into metal housings, into glass tubes, or into ceramic cases the seal must be "tight" enough to prevent passage of vapors, or it must be a true vacuum seal. Low-temperature glasses are, all factors considered, more satisfactory than any other materials.

(f) The properties of bonded crystal groups or masses can often be greatly modified by proper choice of a glass binder. Such properties as hardness, thermal conductivity, and thermal expansion are influenced by the glass bonding agent.

(g) It is sometimes desirable to fuse low-temperature glasses to the surfaces of crystals in order to modify surface characteristics.

ELECTRICAL FUNCTIONS

While practical applications often involve combinations of physical and electrical properties, the electrical functions of low-temperature glasses used as crystal-bonding materials may be isolated in the following ways.

(a) If voids exist in a bonded crystalline material used in a high-voltage field, there is a concentration of electrostatic lines of force at the voids, and corona discharge and arcing occur within the material. The heat developed results in degradation of the insulation and may lead to complete breakdown.

(b) Since water absorption decreases volume resistivity and increases dissipation factor, the glass binder, by filling voids, prevents such absorption. In the case of mica, there is sometimes penetration of moisture along open laminations unless the mica plates are surrounded by glass.

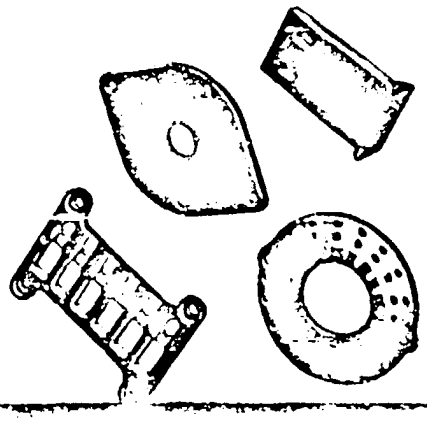
A porous material may be satisfactory in the absence of high-voltage fields and if used in a vacuum or an inert atmosphere, but for most low-loss applications the insulation must be free of voids.

(c) There are instances where the electrical characteristics of a glass-crystal composite must be modified. An example is the case where the dielectric constant must be raised. This can be done by using a glass to bond materials such as titanium dioxide or titanates; and in this instance, as well as others, a high-lead glass aids in increasing the dielectric constant.

REQUIREMENTS FOR LOW-TEMPERATURE BONDING GLASSES

In order to function properly, in terms of the physical and electrical needs outlined above, bonding glasses must meet a considerable number of rather strict requirements, which, taken together, restrict seriously the choices of satisfactory glasses. These requirements may be summarized as follows.

Molded insulators made of synthetic fluor-phlogopite mica and a lead glass binder



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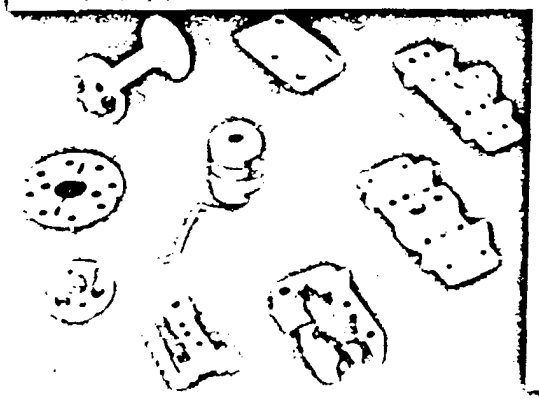
(a) The glasses must be fluid at low temperatures, generally not higher than 1200-1300° F and often below 1000° F.
(b) In addition to fluidity, the viscosity characteristics in certain temperature ranges control the usefulness of glasses.
(c) Surface tension variation with temperature, especially in conjunction with viscosity, may be extremely important in crystal bonding.
(d) For successful crystal bonding, it is essential that the glass wet the crystal. As a rule this involves some degree of chemical reaction although purely physical penetration is conceivable.
(e) Although it is possible for devitrified glasses of certain types (Pyroceram, for example) to have desirable physical and electrical characteristics, the glasses which have proved most satisfactory for bonding crystals do not devitrify when used in the customary manner.
(f) In addition to their function of filling voids to prevent physical absorption or penetration of water, glasses for bonding crystals must have good resistance to chemical reaction with water.
(g) If a glass-crystal composite is to be used for electrical insulation, the glass binder must have low dielectric losses, except where a high dielectric constant is desired. Even in this latter case the dissipation factor should be low.
(h) For glass-crystal insulations the glass should have high surface and volume resistivities.
(i) The dielectric strength of a glass used for bonding crystals should be high if the composite is to act as an insulator in high-voltage fields.
(j) For many applications, a bonding glass must have good thermal shock resistance. For evaluation purposes, this characteristic must be related to thermal expansion and thermal conductivity, as well as other properties.

Molded switch wafers and other parts made of micro-rite mica bonded with a lead glass



(k) With a few exceptions, the thermal expansion coefficients of glass and crystal should be compatible.
(l) Optical properties of the bonding glass may sometimes be important, particularly in the infrared and ultraviolet portions of the spectrum.
(m) For an increasing number of applications the bonding glass must not change or deteriorate greatly when subjected to nuclear radiations.
(n) If a glass-crystal composite is to be employed for radiation shielding, the glass composition generally is one that contains a maximum of heavy ions, such as lead and barium.
(o) Where low density is a requirement the bonding glass may have to be composed of such elements as lithium, beryllium, and boron.
(p) In those cases where glass-crystal composites are employed extensively (glass-bonded micas, for example), often in relatively large pieces, the cost of the bonding glass must be reasonable.
Consideration of the properties and requirements listed above will indicate the complexity of the problem of developing suitable low-temperature glasses for bonding crystals.

METHODS FOR OBTAINING LOW-TEMPERATURE GLASSES

In the development of low-temperature glasses for crystal bonding all of the recognized methods for "loosening" the glass structure are utilized. These methods, based upon vitreous silica as the most stable glass, are briefly summarized below.
(1) BO_3 triangles replace SiO_4 tetrahedra. If the replacement is complete borate glasses result. If partial, the glasses are borosilicates. When it is necessary to keep the softening temperature low the boron must be well in excess of the silica, and the glasses are more properly called silicoborates.
Substitution of B_2O_3 for P_2O_5 lowers the softening temperature of phosphate glasses.
(2) The oxygen ratio (ratio of oxygen atoms to network-forming atoms) is increased. The effects with silica glasses (for example, P_2O_5 replaces SiO_2) are well known. This mechanism is not applicable in the case of B_2O_3 modified with SiO_2 or P_2O_5 since the boron remains triangularly coordinated in the presence of tetrahedral silicon and tetrahedral phosphorus. The matter is not of practical importance since commercial low-temperature glasses contain alkalies, alkaline earths, lead, zinc, barium, etc.
(3) The glass-former is replaced by one of larger size or lower valency, leaving the oxygen ratio unchanged. Thus, Si is replaced in part by Ti or Al, or by Pb in high-lead glasses. In most low-temperature glasses, however, Ti and Al are added for reasons of chemical

durability and modification of other properties. Lead plays an important role, as discussed in the following section, but it is rarely one of replacing a network former.

(4) Network modifiers are added or exchanged. Two actions are involved here. First, the addition of any electrovalent oxide (alkali, alkaline earth, lead, zinc, etc.) increases the oxygen ratio. The network former bonds to all of the introduced oxygens, and fewer oxygens are bonded to two network formers (fewer oxygens act as bridges). In the case of pure borate glasses, the addition of electrovalent oxides at first produces "harder" glasses because the borons assume tetrahedral coordination. This action continues up to an oxygen ratio of 1.61 (where theoretically 78 percent of the boron ions are in triangular coordination and 22 percent are in tetrahedral coordination); and above this ratio the added oxygens are non-bridging. The glasses therefore become progressively "softer." The other network modifier action involves the replacement of a modifier by one of higher potential (Na replaced by Li) or by a larger number of modifiers (Na replaced by Na + K + Li).

(5) The oxygens in the network may be replaced in part by fluoride ions. Since the action involves a change in the degree of covalency of the structural units (SiO_4 tetrahedra, BO_4 triangles), the glasses become "softer." The effect on the nature of the bonds is shown below:

Si-O	50% ionic,	50% covalent
Si-F	70% ionic,	30% covalent
B-O	44% ionic,	56% covalent
B-F	63% ionic,	37% covalent
Al-O	63% ionic,	37% covalent
Al-F	79% ionic,	21% covalent
P-O	39% ionic,	61% covalent
P-F	59% ionic,	41% covalent
Be-O	63% ionic,	37% covalent
Be-F	79% ionic,	21% covalent

In general, glasses used for bonding crystals utilize combinations of the five devices discussed above for decreasing refractiveness.

TYPES OF GLASSES

The following classification does not by any means include all possible types of low-temperature glasses. It does, however, assemble a representative cross section of glasses which have been used, or have been proposed, as binders for crystals. In general, these glasses meet necessary requirements for physical, chemical, and electrical properties, although in a few cases the applications are somewhat restricted (absence of moisture, etc.). In certain instances, reaction between glass and crystal is sufficient to alter the glass composition appreciably, and thereby improve properties to the point where the glasses are successful commercially.

Type 1: RO-B_2O_3. The most common glass in this category is PbO-B_2O_3, although BaO-B_2O_3 and PbO-BaO-B_2O_3 are also found. The pure lead borate glass has an excellent combination of physical and electrical properties, although surface electrical properties are somewhat sensitive to moisture. The high specific gravity is occasionally objectionable.

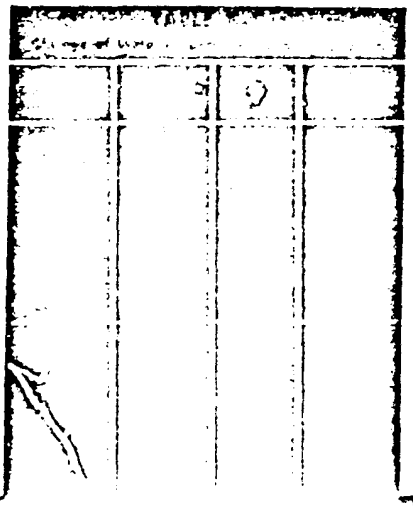
Lead borate glasses of high lead content are used extensively for bonding crystals when the electrical properties of the composite must be considered. Table 8-1 indicates the change of dielectric constant with composition.

Theoretically, no glass is possible above an oxygen ratio of about 3.22 (92 percent PbO, 8 percent B_2O_3). Dissipation factors for the above glasses remain low over most of the range of compositions but tend to increase at the high-lead end. Softening temperatures have not been determined with accuracy, but range from 900-1400° F, with the low temperatures at the high-lead end.

If sufficient time is allowed, these glasses tend to react with crystals, and the compositions may change sufficiently to alter some of the properties.

If fluorine is added to the above glasses in the form of lead fluoride, fluorine replaces part of the oxygen in the BO_3 and BO_4 units, in accordance with the fifth method discussed for obtaining low-temperature glasses. These fluorine-modified glasses soften at temperatures as low as 700° F and are fluid at temperatures not much above 1000° F.

Type 2: RO-B_2O_3-SiO_2. The addition of SiO_2 to a PbO-B_2O_3 or BaO-B_2O_3 glass has the effect of increasing chemical durability. However, the refractiveness



also increases, so that about 10 percent SiO_2 is the maximum permissible if the softening temperature is to be kept below 1200° F. A typical composition is

PbO	52%
H_3BO_3	41
SiO_2	7

If a higher softening temperature is permitted—about 1400° F—the following is satisfactory:

PbO	71%
H_3BO_3	13
SiO_2	16

Type 3: RO-R_2O-Al_2O_3-B_2O_3. The RO is preferably PbO, BaO, or a mixture of the two, although ZnO with PbO is satisfactory. The R_2O may be any of the alkalies, with a mixture likely to give better results. A typical composition (one containing fluorine, however) is the following:

Cryolite	21%
PbO	2
$BaCO_3$	7
$Al(OH)_3$	16
H_3BO_3	54

The softening temperature is about 800° F. Electrical properties are fairly good.

Type 4: RO-R_2O-Al_2O_3-SiO_2-B_2O_3. Again the RO is preferably PbO, BaO, or a mixture; the R_2O is Na_2O, K_2O, or Li_2O, or a mixture. The following is a satisfactory glass:

Feldspar	28%
PbO	28
H_3BO_3	38
Na_2CO_3	6

A composition containing fluorine is

Cryolite	10%
SiO_2	10
Pb_3O_4	30
Feldspar	15
H_3BO_3	35

Still another composition is

H_3BO_3	35%
PbO	30
SiO_2	10
Cryolite	10
Feldspar	10
Na_2CO_3	5

Softening temperatures are in the neighborhood of 1300° F. Electrical properties are good.

Type 5: R_2O-RO-SiO_2. The following glass, which is fluid at 1300° F, is representative of this group:

K_2O, Na_2O, Li_2O	7%
BaO, PbO	52
SiO_2	41

Type 6: R_2O-RO-B_2O_3. The following glass is useful for bonding crystals, but the high alkali content produces high dielectric loss, and surface resistance is not good in a humid atmosphere.

$Na_2B_4O_7$	72%
K_2CO_3	14
CaO	14

Type 7: R_2O-RO-P_2O_5. The following glass, reported in the literature, has a high alkali content (45.3 percent Na_2O), which makes it unsuited for applications where humidity is even moderate. Electrically, it is poor because of the high alkali.

$NaPO_3$	75%
Na_2CO_3	12.5
CaO	12.5

Type 8: RO-B_2O_3-P_2O_5. The high alkali content of the glass below is disadvantageous. It could, however, be used in a dry atmosphere:

Monobasic sodium phosphate	33%
Borax	67

Type 9: ZnO-B_2O_3-V_2O_5. A number of glasses of this type have been made. The V_2O_5 (up to 20%) lowers the softening temperature appreciably. These glasses have thermal expansion coefficients of 45-50 x 10^{-7} per centigrade degree. The softening temperatures are as low as 1160° F.

Type 10: R_2O-RO-R_2O_3-SiO_2-P_2O_5. If phosphoric acid is combined with asbestos, steatite, or mica, and the mixture is heated, a glass of this general type appears to be formed. The bonding is reasonably good, but little study has been given to the mechanics of the bonding action.

SUMMARY

The number of glasses available for bonding crystals is large. Most of them fall into the general categories discussed. Many variations are possible for each type, and the compositions given are merely typical. With all types the addition of fluorine lowers the softening temperature, and thus doubles the number of types. The choice of a glass for bonding crystals is determined not only by the softening temperature. Moisture resistance, dielectric losses, thermal expansion, specific gravity, manufacturing process, and other factors are often governing considerations.