Electrocomponent Science and Technology
1975, Vol. 2, pp. 163–199

A REVIEW OF SOLDER GLASSES

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(Received June 16, 1975)

A compilation of data on solder glasses from the literature is presented. Sources are: Chemical Abstracts, Ceramic Abstracts, Abstracts in Physics and Chemistry of Glasses, and pertinent books. Even though not exhaustive, domestic and foreign sources are included.

INTRODUCTION

Data on solder glasses are scattered throughout the technological literature, but primarily throughout the patent and trade literature of glass manufacturers. In most cases, even in the past reviews, the compiled information was concerned with the solution of specific engineering projects[1-11].

Primary sources for this review were: (a) Chemical Abstracts, (b) Ceramic Abstracts and (c) Abstracts in Physics and Chemistry of Glasses published back to 1948. From these primary sources and from pertinent books,[2,12,13] 81 articles and 88 patents were abstracted. The review is an attempt to bring together (from domestic and foreign sources) as much information on solder glasses as possible. Although it is not exhaustive, the author has attempted to cover by far the greater portion of the pertinent literature.

The review is organized in three sections:

1. A general discussion of solder glasses based primarily on information available in the technical literature.
2. A compilation of vendor data on commercially available solder glasses.
3. A survey of the patent literature.

1 LITERATURE SURVEY OF SOLDER GLASSES

1.1 General

The term solder (or sealing) glass is obviously borrowed from metallurgical techniques. It designates a usage rather than a composition or property of the glass. Thus any glass can (theoretically at least) function as a solder glass, if its properties are such that it forms an adhesive bond between two glasses or between a glass and a metal. The bulk of those glasses referred to in the literature as solder glasses belong to the lead borate or lead borosilicate system. However, other systems can and have been used, and are discussed later in this section.

With few exceptions, present literature (both patent and technical) is concerned with the solution of specific glass-to-metal sealing problems. This is quite understandable from an historical point of view. With the invention and manufacture of light bulbs, glass-to-metal seal technology became an engineering and manufacturing problem of considerable economic importance. It gained increased importance with the mushrooming vacuum tube manufacturing industry.

Glass-to-glass seals were relatively unimportant, and when needed were made by the glass blower using a graded seal when two glasses of different coefficient of expansion had to be joined.[14,15] Only recently has the microelectronics industry in particular posed packaging problems to the design and manufacturing engineer which involve glass-to-glass sealing. Hence the concern of this review.

1.2 Physical Characterization of a Solder Glass

In order for a glass to qualify as a solder glass, it has to meet specific physical criteria. These criteria will depend to a great extent on the properties of the materials the solder glass is to unite. Thus, in general, a good solder glass should have the following characteristics:

1. Low viscosity
2. Thermal expansion matching the workpiece
3. Good adhesion
4. High chemical resistivity
5. High dielectric strength
6. Controllable devitrification or no devitrification

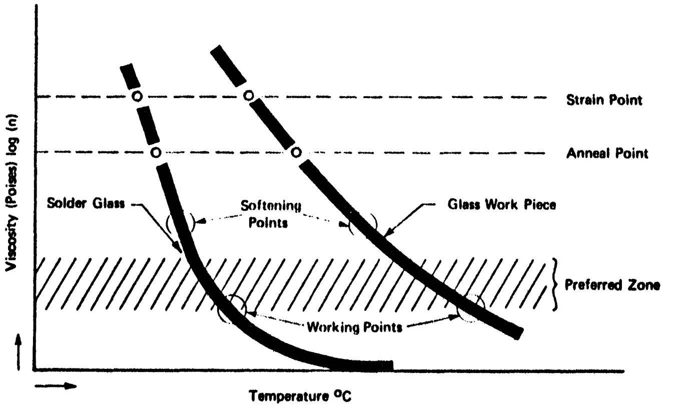


FIGURE 1 Viscosity–temperature relationship of solder glass and work piece.

1.2.1 Viscosity The long viscous range of glasses compared with the sharp melting point of metal solders creates special problems in the use of solder glasses. Like metal solders, solder glasses must have a low viscosity or high fluidity at temperatures which leave the work piece (be it metal or glass) unaffected. The "working point" of the solder glass should be less than or at the most close to the annealing point of the workpiece.[16] In other words, the viscosity of the solder glass at the soldering temperature should be ~ 10^5 to 10^6 poises while the viscosity of the glass workpiece should not be less than 10^{13}. In addition to having good flow characteristics, the solder glass should be quick setting; i.e., it should have a steep viscosity vs. temperature curve (Figure 1). Because glasses can be described as "super cooled" liquids and can "flow" even at room temperature, the rate at which the glass flows is not only a function of temperature but of time and load (or pressure). This pressure can be exerted by the weight of the glass itself.

Figure 2 demonstrates that by slightly increasing the soldering temperature, a considerable reduction in the sealing time (time for the solder glass to spread properly to form good hermetic seal) can be achieved. The reverse does not work so favorably. Unfortunately, it is usually more important to reduce the sealing temperature. For glass-to-glass seals, the advantage gained by a slight reduction in sealing temperature can easily be lost by the prolonged times required, and some deformation of the workpiece. (A study of the pressure-time-sealing temperature relationship of glasses could provide useful technical information.)

1.2.2 Thermal expansion Unlike most metals and alloys, the thermal expansivity of glasses is not linear.[17] For most practical purposes, however, it can be considered linear up to the transformation point (Figure 3), but certainly not beyond. Furthermore, the transformation temperature itself changes with the heating rate.[18] The linear thermal expansion (TE) is schematically plotted in Figure 3 and temperature points of particular interest are identified along with the viscosities at these temperatures.

Above the transformation point (T_g) the glass is

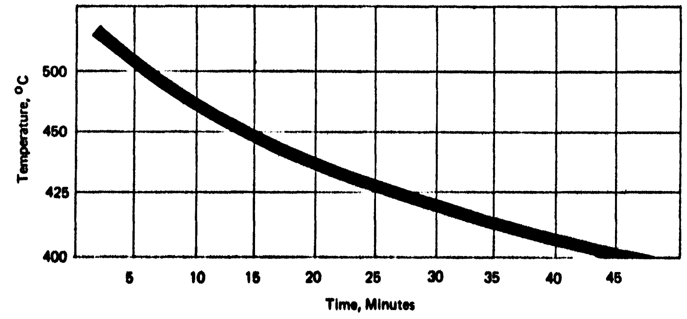


FIGURE 2 Sealing time vs temperature for a typical solder glass.

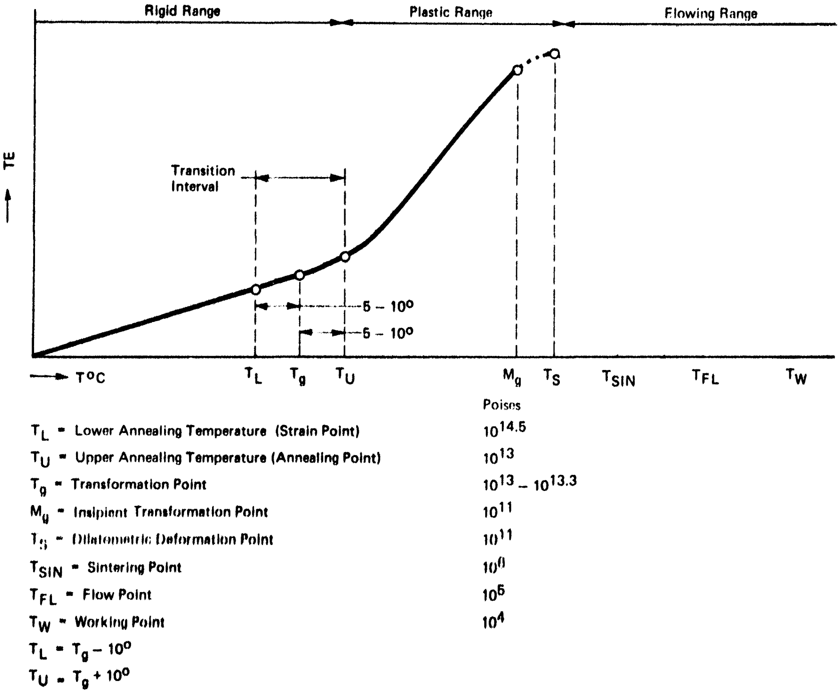


FIGURE 3 Thermal expansion (TE) and relevant viscosities vs temperature of glass.

still plastic and on cooling does accommodate itself to the thermally induced changes in the work piece.[1,2] As the cooling process continues to T_g, the solder glass becomes rigid and brittle. On further cooling to room temperature, considerable cracking of the solder joint can occur if the contraction rate of the work piece and solder glass differ considerably.[1,2,12,13] Obviously, then, to obtain strong, stress-free seals, the coefficient of thermal expansion (CTE) of work pieces and solder glass should match in the temperature range from the stress point to room temperature.[19] Fortunately, because this is rarely possible, a certain amount of mismatch can be tolerated (Figure 4). While the tolerable difference in the CTE's to some extent depends on the geometry of the seal and its use, acceptable limits reported in the literature[16] for "average conditions" are $\pm 2 \times 10^{-7}/°C$, although mismatches of 1 to $6 \times 10^{-7}/°C$ are still acceptable.

Other studies[14,19,20] indicate that when the

Differential CTE is:	*seals are:*
$1 \times 10^{-7}/°C$	excellent
1 to $5 \times 10^{-7}/°C$	satisfactory for medium seals
5 to $10 \times 10^{-7}/°C$	critical stress
$10 \times 10^{-7}/°C$	failure

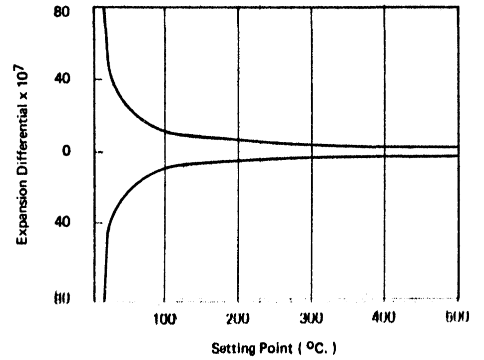


FIGURE 4 Permissible CTE mismatch vs. setting temperature for solder glasses.[16]

Thermal shock, as indicated previously, is a function of the cooling rate and the thickness of the glass layer. Thus, thin layers will withstand thermal shock better for a given CTE mismatch than thicker layers. The thermal endurance of any joint is approximately inversely proportional to the CTE.[21] A poor match between solder glass and workpiece can at times be overcome by designing a compression seal, since glass only fails in tension.[14] Because the soldering of workpieces usually involves the joining of different

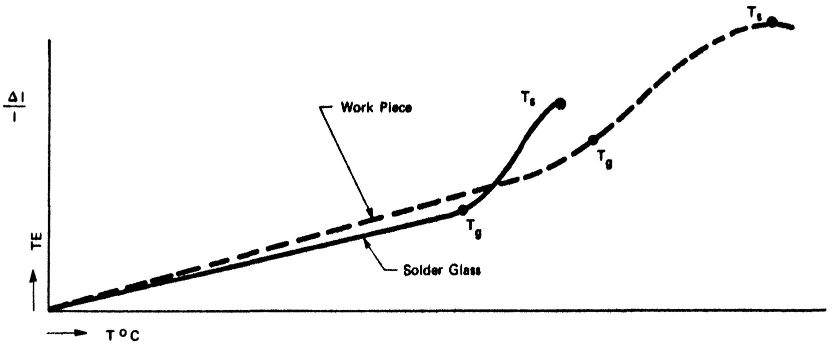


FIGURE 5 Preferred relation of TE curves of solder glass and glass work piece.

materials, the CTE of the solder glass is a very essential parameter. For flat glass-to-metal seals, the conditions prevail that when the CTE metal > CTE glass, the glass is under compressive stresses; when the CTE metal < CTE glass, the glass is under tensile stress.[12,20,22–25] The total stress picture prevailing in a glass-to-metal seal is far more complicated than in the case of fusion of two different pieces of flat glass; axial, radial and tangential stresses must be taken into account. This is extensively discussed both by Volf[2] in his chapter on "Sealing Glasses" and by Kohl[12] in the chapter on "Glass-to-Metal Seals."

In order to obtain strong seals with a minimum of stress when a solder glass with matching CTE (to the workpiece) cannot be found, a solder glass should be selected which meets the following condition: TE solder < TE workpiece (Figure 5). In the case of joining two glass panels, each having a different TE curve, it is desirable to choose a solder glass with a TE curve lying between that of the other two curves and closer to the curve with the lower values (Figure 6).

In choosing a solder glass with an appropriate TE, the range of greatest interest is the contraction range from the "set point" temperature to room temperature. The set point temperature is a function of the seal geometry, rate of cooling, modulus of elasticity, and the viscosity of the glass.[1,2] The set point temperature is vaguely defined on the TE curve as 1/4 to 1/2 the distance from the anneal point to the strain

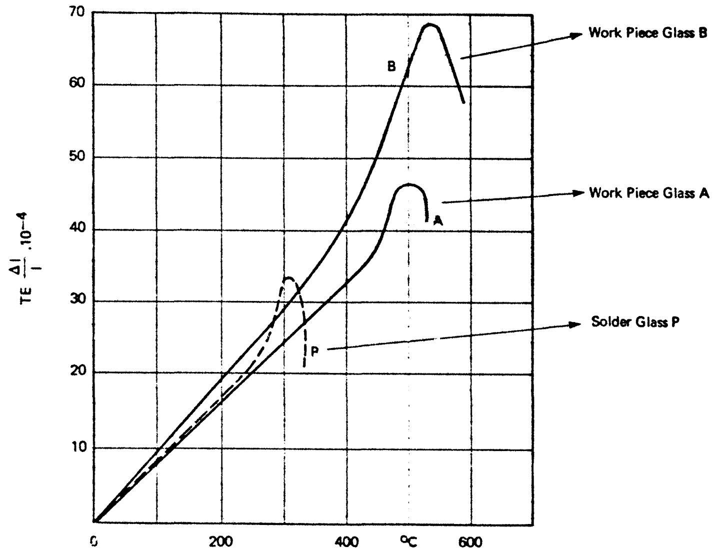


FIGURE 6 Preferred relationship of TE of solder glass curve to work piece TE curve with non-matching TE's.

point'[16] or somewhat more definite "as 5°C above the strain point".[19] Thus holding the glass at a specific temperature or for a prolonged time in the transformation range and then cooling it quickly causes this temperature to become the set point.[22]

Because of its importance, the CTE is frequently used to classify solder glasses. One such classification establishes three categories:[26]

1) Hard Solder Glasses CTE $< 25 \times 10^{-7}/°C$
2) Semi Hard Solder Glasses CTE $= 25 - 50 \times 10^{-7}/°C$
3) Soft Solder Glasses CTE $> 50 \times 10^{-7}/°C$

A more useful classification separates solder glasses into six groups which correspond to the CTE of the most frequently used metals.[23] In this review, this latter classification was expanded to eight groups when classifying the solder glass patents in Section 3.

Because the effect of changes in the molecular composition of the glass on the CTE is very important, several authors have derived equations for the calculation of CTE's from glass composition data. These factors were only applicable for the range of compositions for which they were derived.[27] Sun and Silverman[28] proposed factors for different oxides in glass making. Appen[29] developed an equation for high silica glasses, though it fails for low silica glasses.

1.2.3 Adhesion A strong bond between the solder glass and the workpiece implies optimizing adhesion between the two materials. Adhesive bonds obviously can be mechanical as well as chemical, or both. Published data on adhesion between glasses is very often contradictory. Studying the adhesion of borosilicate and soda lime glass to iron, Ikeda and Sameshuma[30,31] proposed a chemical mechanism (oxyobridges) in borosilicate, but a mechanical mechanism in soda lime glass. In a later publication, Sameshuma[32] then stated that the Fe-soda lime bond is both chemical and mechanical. A roughened surface is reported to improve any glass to metal adhesion.[19] Whatever the nature of the bond, the glass at the soldering or work temperature must first wet the surface of the workpiece before any adhesion can take place.

In the case of metals, which ordinarily are coated with a thin film of native oxide, wetting by a glass is greatly enhanced when the oxide has some solubility in the glass. Borate glasses and low melting alkali glasses – most frequently used as solder glasses – are basic in nature thus a chemical attack is possible in some cases. Dissolution of the oxide on the metal or etching the surface of the glass workpiece aids in spreading the solder glass over the surface, or in other words, it lowers the interfacial surface tension of the original work-solder glass surface.[20,21,33,34] Obviously, the surface of the workpiece must be clean of contaminants. On metals, the thickness of the native oxide layer is critical; at a certain thickness – depending on the oxide – a mechanically weak bond is formed and the seal fails, but if insufficient oxide is present, the solder glass may not form adequate bonds either.[12,22,24]

A word of caution, however, is in order when studying surface characteristics of glass/metal, glass/ceramic or glass/glass interfaces by contact angle measurements. The familiar Young equation, $\gamma_L \cos \vartheta = \gamma_S - \gamma_{SL}$ assumes that the liquid and solid do not interact nor does any mutual solubility exist between the two. These restraints obviously do not apply to the above mentioned interfaces when molten glass is the liquid forming the contact angle. On the other hand, useful information of a practical nature has been obtained from glass contact angles.

To determine the wetting characteristic of solder glass to a given substrate, measurements of the contact angle of the molten glass on the specific substrate has been reported.[20,33,34] Espe recommended a static technique.[33] The contact angle was measured as a function of time at a particular temperature (preferably at the soldering temperature on the substrate in question (Figure 7). A dynamic technique was proposed by Broukal.[20] Employing a motion picture camera and a high temperature contact angle goniometer, the glass contact angle was determined as

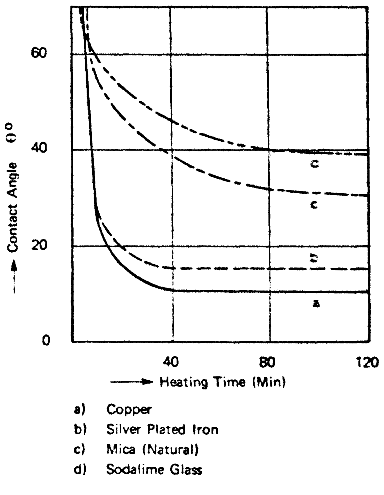
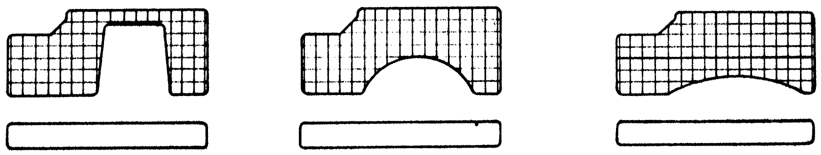


FIGURE 7 Contact angle of Zn–Pb borate glass on various substrates.[33]

a) Shadow Graph of Contact Angle of Glass on Substrate



b) Temperature Dependence of Glass Contact Angle

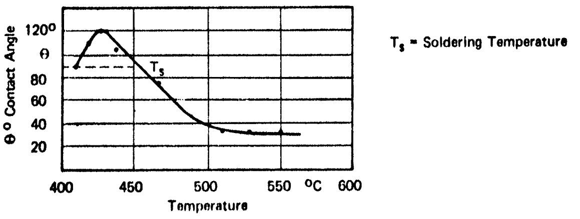


FIGURE 8 Glass contact angle measurements selected to illustrate the progression of the contact angle with temperature.[20]

a function of temperature (Figure 8a). The temperature on the downward leg of the curve at 90° was defined as the soldering temperature (Figure 8b); Aoka[35] called it the sticking temperature; at this temperature the glass begins to wet the substrate. With this technique, Broukal studied the effect of increasing the B_2O_3 content on the soldering temperature at constant PbO content in a $PbO–ZnO–B_2O_3$ glass (Figure 9).

Hussmann[36] suggested that wetting of refractories by metals is a consequence of an electron exchange ($S \rightarrow d$) of the two materials. Studying changes in the contact angles of molten copper on a series of borides and carbides, he proposed that these changes are proportional to the product of the number of d-shell electrons (of the transition metal forming the boride or carbide). While this "quantitative" approach is not immediately applicable to glass, it could support Weyl and Marboe's[37] contention that a dynamic interpretation of the adhesion problem based on the changes in the polarizability of the atoms involved is preferable. Thus approaching the adhesion phenomenon of glasses via dispersion force contribution to the surface energy could be more useful in studying various surface conditions and has been used for such purposes.[38]

From a knowledge of the contact angles, the force of adhesion can, at least theoretically, be calculated by either one of the two formulas:

1) $Wa = \gamma_{gl}(1 + \cos\theta)$

2) $Wa = 2\sqrt{\gamma_{gl}^d \gamma_s^d}$

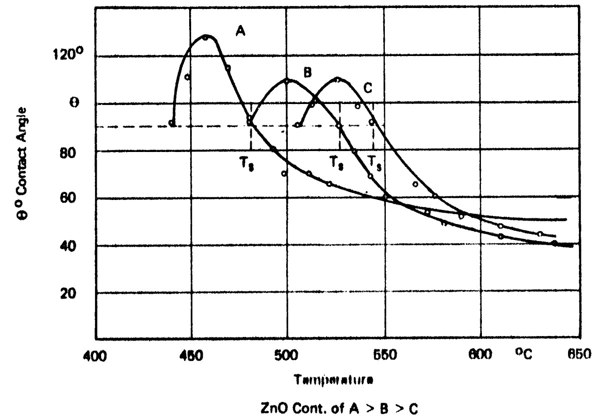


FIGURE 9 Contact angle vs. temperature curves of Zn–Pb borate glass.[20]

where Wa = work of adhesion, γ = total surface energy, the subscripts gl and s mean glass and substrate respectively and the superscript d means dispersion force contribution (in this case to the surface energy). Values of γ^d can be derived from contact angle measurements.[40] Although these equations have been successfully used for non-polar liquids on low energy surfaces, this author has made some trial calculations of metal-glass systems and obtained "work of adhesion" and "interfacial tensions" which were within 10% of values published by Kingery.[41] These results appear encouraging, though this is still a gross over-simplification of the glass/metal interface, but possibly a reasonable first approximation.

Other techniques have been proposed for measuring adhesion of glass-metal systems; these are either peel tests[42] or scratch tests.[43–45] A technique based on measuring the attenuation of ultrasonic energy has been devised. However, none of these techniques (including the contact angle technique) actually measure the absolute energy of adhesion. This may well be expected since the glass/metal (much less the glass/glass interface) is not a sharp transition of one phase to the other. Rather the glass/metal interface for instance is a transition region with a diminishing metal concentration gradient into the glass surface as shown by several studies.[46,47] It is therefore questionable what is really measured by the above techniques. Failure between a glass/metal bond invariably occurs in the glass adjacent to the interface. It has never been reported to occur at the "interface" for glass to metal when the glass was cleaned prior to the metal deposition.

Nevertheless, for engineering purposes, a pull test of some sort could be adequate to test the strength of a glass-to-metal joint. Meier[24] has claimed improved adhesion in glass-to-metal seals when the metal seals were precoated with a thin layer of such metals as Cr, Cu, In, Ag, or Au.

1.2.4 Chemical resistivity Strong hermetic seals with solder glass can be obtained by minimizing reboil and the metal, in glass-to-metal seals should not emit gases at the work temperature.[14,26] Table I gives an indication of the chemical durability of various glasses. Since most solder glasses are essentially of the Pb-borate type, their resistance to chemical attack low compared to other glass types. Glasses of binary compositions of plumbates, borates and phosphates are hygroscopic.[7,8] While the resistance to attack by water can be improved by the addition of oxides of Zn, Zr, Si and Al other properties suffer, i.e. softening point, CTE and devitrification.[9,10,20,21,25,48–50] Various surface treatments such as siliconizing is well known to

TABLE I
Chemical durability of glasses.[15]

Type of Glass	Powder Tests		Weight Loss Tests, mg/sq cm		
	Am. Pharm. Soc. (Distil. H_2O), % Na_2O extracted	ASTM–A ($\frac{N}{50}$ H_2SO_4), % Na_2O extracted	5% HCL (24 hr, 212 F)	5% NaOH (6 hr, 212 F)	$\frac{N}{50}Na_2CO_3$ (6 hr, 212 F)
Silica Glass	—	—	—	—	—
96% Silica Glass	0.0003	0.002	0.0004	0.9	0.07
Soda–Lime — Window Sheet	—	—	—	—	—
Soda–Lime — Plate	0.03	—	—	0.8	0.18
Soda–Lime — Containers	0.05	0.03	0.05	0.8	1.5
Soda–Lime — Lamp Bulb	0.09	0.04	0.01	1.1	1.1
Lead Glass — Electrical	0.07	0.15	0.02	1.6	0.25
Lead Glass — High Lead	0.0006	—	disintegrated	3.6	0.81
Alumino–Borosilicate–Apparatus	—	0.005	—	1.0	0.13
Borosilicate — Low Expansion	0.0025	0.005	0.0045	1.4	0.12
Borosilicate — Low Elect. Loss	—	—	0.02	3.45	0.77
Borosilicate — Tungsten Seal	0.13	—	Completely leached	3.87	1.4
Alumino–Silicate	0.003	0.06	0.35	0.35	0.17
Special — Alkali–resistant	—	0.05	0.008	0.09	0.03

Source: Copyrighted Material From Revised New Edition of "Glass Engineering Handbook", by E. B. Shand, Corning Glass Works, Published by McGraw–Hill Book Co., New York.

improve the glass resistivity towards water. Schroeder[51] discussed surface effects and surface structures as well as the effect of surface damage on the glass.

Mineral acids and water attack borosilicate glasses differently than aqueous bases.[21] The latter not only leach out the alkali ions but dissolve the remaining silica gel which the acids would precipitate.

1.2.5 Electrical properties For most applications, the electrical conductivity of solder glass is not a problem. However, for metal/glass/metal seals, it can be when an electric potential is impressed on it. Meir[24] reported electrolytic decomposition of Pb solder glass in such a seal. Pb was plated out on one metal electrode while the other corroded when a sufficient potential was placed across the seal.

1.2.6 Devitrification Since all glasses can be considered to be supercooled liquids, they are in a metastable state at room temperature. Therefore they all devitrify when heated for a specific time at a temperature below the liquidus.[52-54] The rate at which this devitrification takes place varies greatly. For the majority of the commercially useful transparent glasses, this rate at room temperature is so slow that for all practical purposes it is zero. However, for many glasses, especially glass-ceramic systems,[53,55] it is appreciable and increases rapidly on heating. Because solder glasses must be heated during application, devitrification in such cases becomes a very important consideration. It is convenient, therefore, to separate solder glasses into two general categories:[19,52] (1) Vitreous solder glasses (2) Devitrifying (crystallizing) solder glasses.

The thermal behaviour of these two types of solder glasses is somewhat analogous to that of thermoplastic and thermosetting polymers respectively. Thus:

1) The vitreous solder glass can be repeatedly reworked while maintaining the same characteristics and properties of the original glass composition.

2) On initial curing, devitrifying solder glasses form crystal nuclei and thus a two-phase system. These glasses are stable at temperatures below the softening point, but above that temperature they not only commence to flow but to crystallize as well. The crystallization rate will depend on the temperature, type of glass composition, mode of preparation, and the prehistory of the glass.[7,8] The nucleation rate and the rate of crystallization are considered important parameters of devitrifying glasses. The latter determines the crystal type and receives primary attention[52] since the nucleation rate is largely determined by the thermal prehistory. As the crystallized phase increases, the viscosity drastically decreases and often the CTE. Thus curing times and schedules for

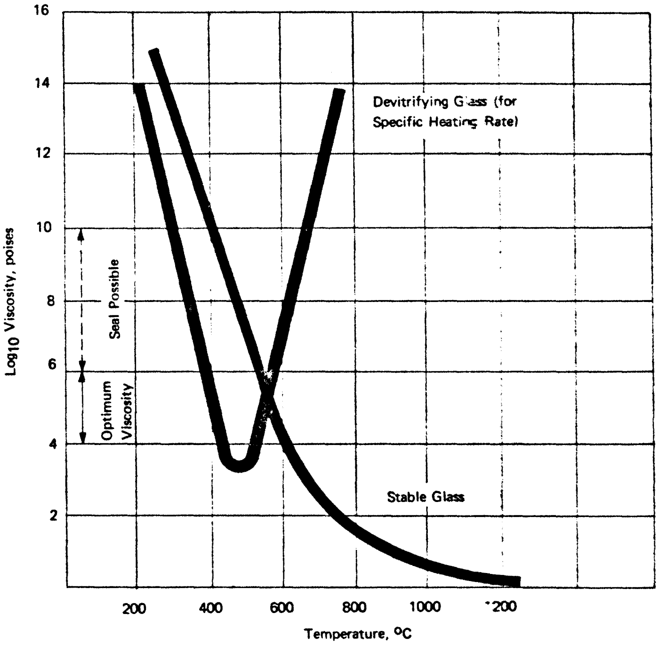


FIGURE 10 Viscosity vs. temperature for a stable and devitrifying solder glass.

these glasses are rather critical, because these parameters determine the number as well as type of crystal nuclei,[55] and thus permit control of the nucleation and the glass properties. When devitrification is desired, the objective is to thoroughly crystallize the glass with a minimum of distortion.[56] That means at as low a temperature and as fast as possible. Figure 10 compares schematically the viscosity changes as a function of temperature of a vitreous and devitrifying glass. The advantages and limitations of devitrifying solder glasses are described in a number of studies.[3,52,56]

There are a number of advantages of the devitrifying solder glasses:

1) Greater joint rigidity is attained at high temperatures.

2) Lower effective thermal expansion is obtained.

3) Thermal expansion maintains compressive stresses more readily in the solder glasses.

4) Lower fillet stresses can be attained.

However, there are also a number of limitations of devitrifying solder glasses:

1) Sufficient flow for a desirable seal may be difficult to achieve.

2) The range is narrow (sometimes too narrow) for sintering prior to crystal growth.

3) Sealing techniques are usually limited to powdered glass technology.

4) Glass quality is usually more difficult to control

5) The final seals are opaque.

Table II demonstrates some of the above points, comparing the ranges of the properties of the two types of commercially-available solder glasses.

Knowledge of the reaction kinetics would be important in choosing a solder glass. Unfortunately, it seldom is available. Some mechanical dispersions of an additive phase can offer the advantage of devitrification by reducing the CTE without increasing the softening point or the transformation point.[57] The author could not find any relationship between devitrification in Pb–Zn borate glasses and the specific surface of the precipitated crystals when adding SiO_2, ZrO_2 or Eucryptite. If the rigid inclusion in a glass ceramic system has a higher elastic modulus than the matrix, the elastic modulus of the composite will increase as the crystal content increases. Thus as much as a 150% increase over the strength of the unmodified glass has been reported.[57]

TABLE II

Thermoplastic and thermosetting solder glasses.[25]

THERMOPLASTIC

Corning Code Number	Expansion Range	Sealing Range	Maximum Service
1826	50– 55 X 10^{-7}/°C	700–800°C	450–500°C
7570	90– 95	500–550	350–400
8363	105–110	400–450	300–325
9776	130–140	350–400	275–300

THERMOSETTING

Corning Code Number	Expansion Range	Sealing Range	Maximum Service
7574 (No. 45 Cement)	40–50 X 10^{-7}/°C	750–775°C	700–750°C
7575 (No. 89 Cement)	80–90	425–450	450–475
7572 (No. 95 Cement)	90–110	425–450	450–475

Forbes[57] also reported that these glasses are self-crystallizing and the maximum content of 2% SiO_2 and 15% ZnO is significant and critical for devitrification. The devitrification tendency is unfavourably reduced by addition of SiO_2 or Al_2O_3, be it deliberate or the result of corrosion product contamination from the crucibles.[3]

The addition of up to 5% P_2O_5 to a Pb-Zn-borate glass enhances the devitrification process without effecting the CTE, though it does increase the deformation temperature.[49] Generalizing about the influence of any component on the devitrification behaviour is hazardous to say the least, unless the base glass system and preferably its thermal history are well defined. Nevertheless, some generalities have been reported by Knapp:[7,8] in the case of borosilicate glasses, devitrification tendencies can be reduced by increasing the alkali or Al_2O_3 content or decreasing the CaO or MgO content. Knapp also reports that monovalent oxides cause the crystallization of trydimite, whereas divalent oxides favor the formation of crystobalite. If the ratio in a borosilicate glass of $B_2O_3/SiO_2 > 1$ the rate of crystal growth remains constant. But a ratio of Al_2O_3/MgO between 0.33 to 0.50 slows down crystallization and narrows the temperature range in which crystallization occurs. Furthermore, devitrification can be catalyzed by the cooling melt in contact with crucible material (i.e., Pt).

1.3 Effect of Chemical Composition on Solder Glasses

It is desirable to have working temperatures of a solder glass as low as possible. Unfortunately, the term "low melting" glasses in the literature may mean any temperature between 100°C to 900°C.[58] Table III gives a general idea of the type of glass, their solder temperature and CTE. On the other hand, Bischoff[59] designed as low melting glasses wt. compositions of SiO_2 5 to 50%, B_2O_3 5 to 90% and PbO 33 to 90% with a softening point of 370 to 890°C.

There is a considerable amount of information published in the literature – mostly in the patent literature – on the effect of composition on solder glass properties. These efforts are being far from systematic; i.e., each investigator addressing himself to the solution of a specific problem evaluating usually one or the other parameter only. Most of the glasses are multicomponent systems thus studies of phase diagrams are prohibitively complex. A systematic study is further complicated by the fact that even a small amount (1%) of constituents can effect such properties as phase separation and microstructure.[11,50] Therefore, extrapolation from one system to another, even to a similar one, is at best a risky practice. This undoubtably accounts for the large number of patents and confusion in areas which on the surface appear to be rather similar. Given these words of caution, the following will be an attempt to summarize the published work in this area.

In general, for silicate glasses, the addition of alkalies PbO, B_2O_3 up to 15% and Al_2O_3 increases the viscosity while addition of MgO, ZnO, CaO and Fe_2O_3 decreases it. The effect of these modifiers is by no means uniform over the entire temperature range; i.e., alkalies have a minimum viscosity particularly in the low temperature range while CuO increases the viscosity more than any other oxide and

TABLE III

Low melting solder glasses.[58]

Glass Type	CTE X 10^7	Deformation Temp °C	Solder Temp °C
Pb – Tellurite	170–180	260–300	400–450
Pb – Borate	75–120	280–430	425–559
PbZn – Borate	70–110	320–450	450–570
PbCd – Borate	80–90		500–550
Pb – Borosilicate	40–120	370–700	500–900
PbZn – Borosilicate	75–80	370–100	500–550
Pb – Aluminoborate	60–85	440–485	550–650
Li – Aluminoborate	60–100	370–515	500–650
Pb – Aluminoborosilicate	80–95	390–440	520–600
NaZn – Borophosphate	50–150	300–450	450–600
CdZn – Borofluorophosphate	~ 50	500–550	620–680
Zn – Borovanadate	~ 50	500	620
As–Te–S	170–420	25–200	
As–S–J	300–490	48–160	177–400

especially at low temperature. At higher temperatures CuO first decreases and then increases the viscosity again.[12] Unfortunately, a decrease in the viscosity is usually associated with an increase in the CTE. This result might be expected on theoretical grounds. Since the predominant structure of lead-borosilicate glasses is a rigid network,[60] any component which breaks this network or acts as a chain terminator (like modifiers) will permit the "clumps" of residual sections of the network to move under a stress gradient and thus lower the viscosity. However, because of the improved mobility, thermal expansion will increase and with it the CTE. The bulk of the solder glasses presently employed belong to the systems of zinc-lead-borates or lead-borosilicates. Modifications of these glasses were made by additions and variations in the network formers and modifiers as well as in the intermediate oxides.[54]

In the high lead (80%) borosilicate system, addition of a) Ag increases the devitrification tendencies; b) ZnS or CdS imparts phosphorescence to the glass; c) up to 4% BaO improves the adhesive strength to metals; and d) up to 1% alkali oxide raised the value of CTE.[25] The same system was studied by Dale *et al.*,[9,10] and Broukal.[20] Their results are summarized in Table IV. Dale *et al.* reported that addition of fluorides did not markedly change the softening temperature. The composition which provided maximum chemical durability was reported as: PbO 75 to 55%, ZnO 20 to 10%, B_2O_3 25 to 15%, with a deformation temperature of 415 to 500°C; CTE = 78 to 90 x 10^{-7}/°C.

An extensive study of lead-silicates, lead-borates, alkali-borates and Cabol Glasses by Abou-El-Azm *et. al.*[50] can be summarized as follows:

1) In lead silicates (T soft 394 to 672°C) T soft can be decreased by:

a) Reducing SiO_2 content, replacing Pb by alkalies ($Li > Na > K$ in terms of effectiveness).

b) Replacing Si by B.

T soft can be increased by replacing:

a) Pb by alkaline earth ($Mg > Ca > Si > Ba > Zn$) oxides.

b) Replacing Si by Al or Zr.

2) In lead borates (T soft 430 to 508°C), T soft can be decrease by:

a) Reducing B_2O_3 content.

b) Replacing Pb by alkalies ($Li \sim Na \sim K$).

c) Replacing B_2O_3 by Al.

and increased by:

a) Replacing Pb by alkaline earth oxides and ($Mg \sim Zn \sim Ca \sim Ba \sim Sr$).

b) Replacing B by Zr and Ti ($Ti > Zr$).

3) In alkali borates (T soft 355 to 545°C), T soft is increased by additions of:

a) Alkalies (Li Na K) of even small amounts (0.2%).

b) Al_2O_3, MgO, ZnO

c) Decreasing the B_2O_3 content.

TABLE IV
Influence of glass composition and properties.[20]

Component Kept Constant	Component Being Increased or Substituted			Properties Influenced				
	Pb O	B_2O_3	ZnO	CTE	T_{SOFT}	Devitrification Temp	Deformation Point	Soldering Temp
ZnO	+			INC			DEC	DEC
Pb O		−	+			INC		DEC
B_2O_3	+		−					DEC
Zn O	B_2O_3			DEC	INC			
Pb O		Zn O				DEC		
ZnO		Pb O				DEC		
B_2O_3			Pb O		DEC	DEC		
B_2O_3/ZnO	+			INC			DEC	
Pb O		−		INC			DEC	

4) In Caboal glasses (Ca-B-Aluminates)(T soft 550–794°C), T soft can be raised by:

a) Replacing B_2O_3 by Al_2O_3 or CaO (Al > Ca).

b) Replacing CaO by ZrO_2, TiO_2, SiO_2 (Si > Zr > Ti).

T soft can be decreased by:

a) Replacing CaO by alkalies (Li > Na > K).

b) Replacing alkaline earth oxides.

The effect-considerable on viscosity, minimal on CTE – resulting when substitutions were made of a noble-gas-type ion (i.e., Mg^{2+}) or a non-noble-gas type (Cu^{2+}) in high silica (67 mole %) glasses were reported by Karkhanavala et. al[27] These authors followed the approach pioneered by Weyl;[61] i.e., relating the physical properties of the glass to the polarizability of its ions and their electrical shielding requirements. Cu_2O is known to reduce the softening temperature in silicate systems.

In the P-Zn-Borate systems, Knapp[8] reported; (a) Replacing ZnO by CdO up to 40% did not cause devitrification but apparently reduced the melting point, (b) additions of 4 to 10% Li_2O increased crystallization and (c) Substituting ZnF_2 for ZnO reduced the devitrification tendency as well as the softening point. The solder glass recommended by Knapp is ZnO 50 to 30%, B_2O_3 18 to 20%, P_2O_5 16 to 20%, CuO 14 to 17%, ZrF_2 0 to 11%, with T soft 510 to 550°C and CTE $50 \times 10^{-7}/°C$. Addition of P_2O_5, SiO_2 and Al_2O_3 to Pb-Zn-borate glasses was studied extensively by Shirouchi,[49] whose findings are summarized in Table V. Kruszewski[62] discusses the effect of dissolved gases in optical glasses.

1.4 Miscellaneous Solder Glasses

1.4.1 High elasticity solder glasses. Semenov *et. al.,*[63] reported strong joints using a soda lime glass to seal two glasses together of varying CTE's (91 and 48 $\times 10^{-7}/°C$ respectively). The glass composition recommended was: SiO_2 27%, Al_2O_3 21%, B_2O_3 39%, Na_2O 4 to 2%, K_2O 1%, CaO 8%, MgO 0 to 2%, with a CTE 52.6 to $54 \times 10^{-7}/°C$. This solder glass replaced a graded seal between the Russian glasses BD–1 and ZS5 (their compositions are included by Volf).[1,2] The success of this seal is attributed to the elasticity of the solder glass.

Lap joints that withstood 15,000 psi at room temperature and 3000 psi at 1000°C could be made in a metal ceramic system using 60 to 80% of a sodium-borosilicate glass (Na_2O 0.5%, B_2O_3 57%, SiO_2 38%) plus 40 to 20% of a metal powder such as Cu, Ni or Mn.[64]

1.4.2 Vanadate glasses Glasses based on the vanadium oxide system have low melting points but the CTE can vary over a considerable range. A glass with good IR transmission was reported[65] with a composition of BaO 15%, TeO_2 31.4% and V_2O_5 53.6% having a deformation temperature of 285°C and a CTE of 135×10^{-7}.

Glasses in the composition range B_2O_3 10 to 40%, ZnO 20 to 60%, V_2O_5 10 to 70% are reported[48] to have soldering temperatures of 600°C and CTE's of 45 to 55×10^{-7}. Many of the vanadate glasses have poor water resistance, but addition of PbO, BaO or CaO and Al_2O_3 up to 5% does improve their water resistance. These glasses are actually n-type semiconductors.

TABLE V
Effect of composition in Pb–Zn–borate glass.[49]

Glass Property	Effect of Molar Increase in the Following Components		
	P_2O_5	SiO_2	Al_2O_3
Devitrification	Enhanced	Reduced	Reduced
Surface Hardness	Reduced	Enhanced	Enhanced
Resistance to H Cl	Enhanced	Enhanced	Enhanced
Resistance to HF	Reduced	Enhanced	Enhanced
Resistance to HNO_3	Enhanced	Enhanced	Enhanced
Deformation Temp	Enhanced		
CTE	none		
Adhesion to Steel	Enhanced	Enhanced	Enhanced

1.4.3 Tellurium glasses TeO_2 forms a variety of glasses with oxides of Li, Na, B, Nb, P, Mo, W, Zn, V, Mg, Cd, Ti, Ge, Th, Ta, La, Sb, Bi, V and Pb. These varieties are binary or ternary compositions, and are generally characterized by a high refractive index, CTE, density and dielectric constant but a low deformation temperature.[66]

The virtue of the lead tellurides are high densities (4 to 6 g/cc) and a high refractive index (2.199). The zinc-tellurite glasses (TeO_2 65 to 75%) are reported[67] to have very low tan δ (2.63 to 4.3 x 10^{-3}). These glasses are stable to cold water but attacked by boiling water and dilute acids and alkalies. Additions of 0.5% Cu, 1% Nd_2O_3 or 16% Al_2O_3 if substituted for ZnO does not change the glass properties to any extent.

1.4.4 Non-oxide glasses These glasses are based on ternary systems of As–Tl–S, As–Tl–Se, As–Se–S, and As–S–Br,[69] as well as Ce–P–Te, Ge–S–Te, Ge–Se–Te and Ge–As–Te.[66] Umblia[58] and Cooper[66] discussed these glasses extensively; the first from the point of view of solder glasses, the latter emphasizing their electronic device applicabilities. These glasses are very poisonous and chemically very unstable.[70] While as mentioned previously, melting points as low as 100°C are observed, their CTE are extremely high (140 to 420 x 10^{-7}/°C) and their electrical resistivities range from 10^{12} to 10^{16} Ω cm. This combination of properties does not make them useful solder glasses. Yakhkind[71] has discussed binary non-oxygen glasses of higher density (4 to 6 g/cm^3) and high refracting indices (1.9 to 2.2).

1.4.5 Phosphate glasses These glasses are soluble even in cold water[72] and in addition, their CTE's are very high; i.e., 215 to 289 x 10^{-7}/°C, though their softening temperature are low (270°C) for the alkaliphosphates[73] and for aluminium orthophosphates (CTE = 159 x 10^{-7}/°C with a softening temperature of 330°C).[74] Zinc-borophosphate glasses (ZnO 68.4 mole %, B_2O_3 22.4 mole %, P_2O_5 9.5 mole %) have a low CTE (50 x 10^{-7}/°C) and softening temperature of 579°C.[75] The chemical stability of these glasses was not improved by the addition of oxides of Zn, Mg, Ba, Cu, Al, Ti, Zr, Si and Pb.

1.4.6 IR Absorbing solder glass A Te-V glass was mentioned previously. Addition of 1 to 8% of Cu to a lead-aluminium borosilicate (like Corning 7570 or Pemco QJ207 or XJ208) produces and IR absorbing solder glass compatible with regular lead glasses.[76] This glass was developed because the usual IR absorbing sealing glasses containing Fe are not compatible with lead glasses.

1.4.7 Electrically conducting solder glasses The electrical properties have been studied[77] of glass systems based on the oxides of the transition elements (V, Mo, W, Fe, Mn and Ti) in various combinations with oxides of alkali, alkaline earth metals, Si, P, B, Al and Zn. The volume resistivities of these glasses ranged from 10^9 to 10^{13} Ω cm; unfortunately, no other data is furnished. Bartuska[78] described the formation of a seal by melting an electrically conducting solder glass in the phospho-vanadium system in situ by passing a current through the work and solder glass. The conduction mechanism is by electron conduction and the resistivity is a linear function of the vanadium oxide content of the glass.

1.5 *Alternatives to Solder Glasses*

When a suitable glass was not available, other ingenious sealing techniques for glass-to-glass or glass-to-metal have been employed. Metal as well as alloy solders have been used to good advantage, because their CTE's can be more easily matched to the workpiece than that of glass.[26,79] In the case of glasses, thin metal foils can be used or a thin film of metal is predeposited either by sputtering or evaporation on the workpiece. A variety of organic polymers as adhesives of glass joint have been discussed by Escaich.[80] Lees[81] made good cryogenic seals by fusing borosilicate glass (CTE 53 x 10^{-7}/°C) directly to Hafnium (CTE x 10^{-7}/°C).

2. REVIEW OF COMMERCIALLY AVAILABLE SOLDER GLASSES

The data is this section was compiled from several sources – books, journals, and customer information from vendors. It should be pointed out that most of the commercially-available solder glasses were developed to meet the needs of glass-to-metal sealing. To avoid unwieldy compilations of tables, the information will be organized per source rather than by type of glass.

A considerable amount of data on commercial sealing glasses is compiled in three books referred to frequently in Section 1 but should be repeated here because many of these glasses are identified by the vendors code numbers.

a) "Handbook of Materials and Techniques for Vacuum Devices," Editor, W. H. Kohl, Chapter 14 on "Glass-to-Metal Seals." In addition to discussing some commercially available GE and Corning solder glasses, it has extensive information on physical data of metals and alloys commonly used in glass-to-metal seals (pp. 400 to 403). Chapter 14 lists 167 references on the subject, though most of them are on glass-to-metal seals.

b) "Technical Glasses," by M. B. Volf (1961). Unfortunately, this book is out of print. Chapter 15 is entirely devoted to "Sealing Glasses." Again the glasses are arranged according to the metals to be joined to the glass. This chapter lists the composition, properties and commercial code numbers of 168 solder glasses mostly lead-borosilicates. By far, the majority of these glasses are manufactured by European firms including a number from Russia, CSSR and Poland. Chapter 15 lists 69 references on solder glasses, some of which may no longer be on the market. Because it is impossible to list all the compositions, Table VI summarizes the types of properties and uses of these glasses.

c) "Glass-to-Metal Seals," J. H. Partridge (1967). Table VII lists the physical properties of glasses and metals used in seals including vendor and code number of the glasses. In order to relate the old Corning Code numbers used in the previous tables and sources, Table VIII (Kohl[12]) correlates these with the new four-digit Corning glass code.

Subsequent tables are either direct copies or summaries of vendor information both domestic and foreign. These include: (a) Table IX Corning Solder Glasses (b) Table X Listing of Corning and Kimble Glass Codes which are essentially equivalents. (c) Tables XI to XIII, Owens-Illinois (Kimble) Solder Glasses. A comment on these three tables is in order. Kimble has a dual code system. Their glasses are identified by letters plus a digit (i.e., SG–7). However, the preferred computerized order number is an all digit number (in this case 00130). All three tables are reproduced despite some overlap of information. Table XI list those solder glasses especially recommended by the manufacturer for packaging in the electronics industry. Table XII and XIII includes special solder glasses as well, (d) Table XIV lists solder glasses manufactured by the General Electric Co.

Subsequent tables list solder glasses of European manufacturers. All but one of this data comes from

TABLE VI

Summary of Chapter 15 "Sealing Glasses" in *Technical Glasses* by Volf.[2]

Seal to Metal	$\alpha \cdot (10^{-7})$ Glass Line Coefficient of Thermal Expansion	Tg °C	T_{soft} °C	No. of Glasses Listed	Type of Glass
Pt	89-92	504-530		2	Lead
Dumet	88-94	425-475	610-630	15	Lead and Alkali Lime
Envelope of Incandescent Lamps	98	500		2	High Silicon with and without Baria
Fe-Ni-Cu Feanico	91	400-430	619-700	12	Lead, Alumino Silictes, Alumino Borosilicates
Fe-Cu	90-103	400-588	440-696	28	Lead and Alkali Limes and Lead Baria
Fe	112-135		500-540	25	Lead Baria, Lithian and Titanion Lead Glasses
Housekeeper Cu	No Limit			1	Phosphate Glass
Mo	48-52	625-540	700-790	33	Aluminum Borosilicates
Kovar	43	500-560	543-730	25	Borosilicates and Aluminum Borosilicates
W	36-42	530-770	680-800	25	Alkali-Alumino - Borosilicates

TABLE VII

Glass-to-metal seals (J. H. Partridge; Soc. of Glass Techn. 1967).

Combination.	Metal.	$\alpha \times 10^6$ (Metal).*	Glass.	$\alpha \times 10^6$ (Glass).*	Annealing Range (Glass).**		Colour of Seal.	State of Strain (annealed seals viewed at right angles to longitudinal axis).	Diameter of Wire (2a).	Diameter of Sheathed Single Wire Seal (2b).	Ratio b/a.	Maxim Tens Stre (aft norm anneal (kg./c
1a	Tungsten	4·4	Corning 726MX	3·3	553°	510°	Straw to light brown	Severe compression	2·5	7	2·8	480 r
1b	,,	,,	Pyrex	3·2	- -	—	,, ,,	,, ,,	1·0	4·1	4·1	520 r
1c	,,	,,	Corning " Nonex " G702P	3·6	518	484	,, ,,	Compression	2·5	7	2·8	127 r
1d	,,	,,	Corning " Uranium " 371BN	4·1	535	497	,, ,,	Slight compression	2·5	7	2·8	48 r
1e	,,	,,	G.E.C. W1	3·8	550	450	,, ,,	,, ,,	1·5	7·3	4·9	50 r
1f	,,	,,	B.T.H. C9	3·6	530	460	,, ,,	,, ,,	1·0	3·0	3·0	70 r
1g	,,	,,	B.T.H. C14	3·7	730	—	—	Strain free	—	—	—	—
1h	,,	,,	G.E.C. WQ31	1·0	—	—	Bright metallic	Very severe compression	—	—	—	—
2a	Molybdenum	5·5	Corning 705AJ	4·6	496	461	Light brown	Severe compression	2·5	7	2·8	215 r
2b	,,	,,	Corning G71	5·0	513	479	,, ,,	Slight tension	2·5	7	2·8	62 c
2c	,,	,,	G.E.C. HH	4·6	590	500	,, ,,	Compression	1·0	3·9	3·9	30 - 5
2d	,,	,,	B.T.H. C11	4·5	585	500	,, ,,	,,	1·0	3·0	3·0	80 r
2e	,,	,,	G.E.C. H26	4·3	720	600	,, ,,	Severe compression	1·02	3·49	3·4	260 r
3a	Platinum Substitute Alloy (Copper-coated 43% Ni–Fe alloy)	c. 7·8 longitudinal c. 9·0 radial	G.E.C. L1	9·1	435	350	Red	Severe tension	0·8	2·7	3·4	310 c
3b			B.T.H. C12	8·7	430	360	,,	,, ,,	—	—	—	—
3c			Corning G5	8·9	429	404	,,	,, ,,	2·5	7	2·8	387 c
4a	Platinum	9·4	G.E.C. X4	9·6	520	450	Bright metallic	Severe tension	0·8	4·1	4·1	600 c
4b	,,	,,	G.E.C. L1	9·1	435	350	,, ,,	,, ,,	0·8	4·1	4·1	560 c
5a	26% Cr–Fe Alloy	10·2	Corning G5	8·9	429	404	Greenish grey	Compression	2·5	7	2·8	128 r
5b		,,	Corning G6	10·2	—	—	,, ,,	Tension	2·5	7	2·8	126 c
5c	,,	,,	Corning G8	9·2	510	475	,, ,,	Compression	2·5	7	2·8	139 r
5d	,,	,,	" Glass 286 " ‖	10·3	—	—	,, ,,	Strain free	—	—	—	About
5e	,,	,,	G.E.C. L14	9·8	435	350	,, ,,	Slight compression	1·1	3·3	3·0	20 – 6
5f	,,	,,	B.T.H. C31	9·7	442	—	,, ,,	,, ,,	—	—	—	—
6a	Fernico I (54% Fe, 28% Ni, 18% Co)	—	Corning 705AJ	4·6	496	461	Grey	Compression	2·5	7	2·8	118 r
6b			Corning 705AO	5·0	495	463	,,	Slight tension	2·5	7	2·8	52 c
6c			Corning G71	5·0	513	479	,,	,, ,,	2·5	7	2·8	41 c
6d			" Glass 184 " ‖	—	—	—	—	—	2·5	7	2·8	23 c
7a	Fernico II (54% Fe, 31% Ni, 15% Co)	—	Corning 705AO	5·0	495	463	Grey	Strain free	2·5	7·5	3·0	About
7b	Fernico II made by powder metallurgical processes	5·1	G.E.C. FCN	5·1	520	460	,,	,, ,,	1·04	4·33	4·1	About
8	British Kovar type alloys, e.g. "Nicosel," "Telcoseal No. 1" and "Darwin's F" alloys	4·5	B.T.H. C10	4·8	497	—	,,	Slight compression	1·0	3·0	3·0	0—10 (accor to me
			G.E.C. FCN	5·1	500	440	,,	Strain free	2·5	7	2·8	12 r
9a	Fernichrome (37% Fe, 30% Ni, 25% Co, 8% Cr)	9·95	Corning G5	8·9	429	401	,,	Very slight tension	2·5	7	2·8	14 cl
9b		—	Corning G8	9·2	510	475	,,	Compression	—	—	2·8	84 rl
10	50/50 Ni–Fe alloy	9·5	G.E.C. L1 ¶	9·1	440	350	,,	Slight tension	1·04	3·75	3·6	34 cl
11	Copper-coated 50/50 Ni–Fe alloy	9·5	G.E.C. L1 ¶	9·1	440	350	Red	Slight compression	1·05	3·28	3·2	30 rl
12	52% Fe, 42% Ni, 6% Cr alloy	8·9	G.E.C. L1 ¶	9·1	440	350	Grey	,, ,,	1·04	3·9	3·8	30 rl
13	41·5% Ni, 57·8% Fe alloy	—	" Glass 1075 " ‖	5·3	—	—	,,	Strain free	—	—	—	About
14a	Iron	13·2	" Glass 542 " ‖	13·5	—	—	,,	,, ,,	—	—	—	About
14b	,,	,,	G.E.C. R16	11·2	—	—	—	,, ,,	2·02	6·6	3·3	About
14c	,,	,,	B.T.H. C76	11·6	—	—	—	,, ,,	—	—	—	—
14d	Copper-plated iron	,,	B.T.H. C41	12·9	442	—	Red	,, ,,	1·0	3·0	3·0	Less t 10 r
15	Copper	17·8	Many glasses if suitably shaped	3·5–10·2	—	—	Red to gold	Strain-free a fraction of millimetre from joint	—	—	—	—

NOTES.

rl. signifies in radial direction.

cl. signifies in circumferential direction.

* α = mean coefficient of linear thermal expansion between 20° and 350° except for Corning glasses where range is 0—310°.

† Values taken from Hull and Burger's paper.

‡ Values taken from Hull, Burger, and Navias' paper.

§ See list of Corning glasses attached. This, together with thermal expansion data, was communicated by Dr. Louis Navias.

‖ Special glasses made by Dr. Navias. See Table for chemical compositions.

¶ C12 may also be used for sealing to these metals.

** *Annealing Range of Glasses.*

As yet there is no agreed definition of annealing range in terms of the viscosity of the glass. The higher temperature corresponds to the viscosity of about $10^{13 \cdot 4}$ poises. Specimens of glass become substantially free from strain when heated for 15 minutes at the temperature corresponding to this viscosity. Specimens 5—7 mm. in diameter become strain-free on heating to this temperature at 2° per minute. The lower temperature is that corresponding to a viscosity of $10^{14 \cdot 6}$ poises, in the case of Corning glasses, and to a viscosity of about 10^{16} poises in the case of G.E.C. glasses.

Corning Glasses.

Code No.	Glass No.
774	726MX
772	G702P
3320	371BN
705	705AJ
771	G71
005	G5
013	G6
008	G8
706	705AO

Composition of Special Sealing Glasses made L. Navias.

Glass No.	286.	184.	1075.	5
SiO_2 …………	54	65	34	4
PbO …………	29	—	29	3
Na_2O …………	5	7	2	
K_2O …………	8	—	—	1
BaO …………	4	—	—	-
Al_2O_3 …………	—	5	7	-
B_2O_3 …………	—	23	28	-
CaF_2 …………	—		—	

TABLE VIII
Correlation of current four-digit Corning Glass code with obsolete laboratory code numbers.[1 2]

Current	Obsolete	Current	Obsolete
0010	G-1	7210	G-720-Pn
0014	G-14	7230	G-707-GS-1
0041	G-4-D	7240	G-715-AO
0050	G-5	7250	G-720-OI
0080	G-8	7251	G-720-WH
0081	G-124-HD	7252	G-726-XP
0100	G-164-EC	7290	G-167-GL
0110	G-164-HC	7330	G-733-A
0120	G-12	7331	G-108-PN
0240	G-125-BB	7340	G-733-B
0250	G-125-AJ	7500	G-750-AH
0280	G-128-G	7510	G-750-AI
0281	G-128-AQ	7520	G-750-AJ
1710	G-172-RM	7530	G-805-F
1720	G-172-AJ	7550	G-805-G
1723	G-889-AEW	7560	G-750-AL
1990	G-189-IY	7570	G-750-GL
1991	G-184-IY	7720	G-702-P
2473	G-240-PY	7730	G-1752-A
2475	G-240 HP	7740	G-726-MX
3320	G-371-BN	7741	G-726-YM
3530	G-353-GE	7742	G-726-ABE
3540	G-350 Z	7750	G-705-R
4320	G-431-AM	7760	G-720-GO
4407	G-40-D	7780	GT-70
5380	G-534-A	7900	G-790-H
5420	G-542-P	7910	G-790-J
5810	G-570-G	7911	G-798-BE
5830	G-570-AT	7912	G-790-N
5890	G-586-CK	7981	G-707-HN
5911	G-586-EW	7991	G-704-EO
6611	G-61-I	8110	G-813-BJ
6992	G-63-AK	8160	G-814-KW
7030	G-704-BA	8800	G-80
7040	G-705-BA	8830	G-866-LC
7050	G-705 AJ	8870	G-858-V
7051	G-705 FD	8871	G-189 IA
7052	G-705-FN	9010	G-856-DO
7055	G-710 HY	9012	G-171-PA
7056	G-810 MF	9700	G-970-G
7060	G-705-AO	9720	G-970-L
7070	G-707-DG	9730	G-972-A
7120	G-712-O	9740	G-970-HW
7200	G-707 GU-1	9741	G-970-OF
		9820	G-981-TI

TABLE IX
Corning solder glasses (compiled from Corning Product Information).

Glass Code No.	Softening Points	Annealing Points	Strain °C	Linear Thermal Expansion $\alpha\ 10^7/^\circ C$	Density g/cc	Designation	Purpose	Working Pt.	Dielectric Const.
1415	776	654	620	79		Ferrite Sealing Glass	Ferrite Sealing Glass		
1416	463	368	364	81		Ferrite Sealing Glass	Ferrite Sealing Glass		
1417	427	356	336	89		Ferrite Sealing Glass	Ferrite Sealing Glass		
1990	500	370	340	124	3.50	Low Loss Iron	Fe, Ferrite		
3320	780	542	499	40	2.27	Borosilicate	W		
7040	702	489	450	47.5	2.24	Borosilicate	Kovar		
7047	540	400	370	140	2.86	Barium Silicate	Cu/Al Alloy		
7050	703	501	401	46	2.25	Borosilicate	Series Sealing		
7052	712	480	436	46	2.27	Borosilicate	Kovar		
7056	718	512	472	51.5	2.29	Borosilicate	Kovar		
7200	–	645	–	19	–			1100<	
7230	1160	770	688	14	–	Low Expansion	PT & W Wires		
7240	–	555	–	21	–			900<	
7510	705	517	478	50	2.34	Series Sealing			
7520	755	571	529	60	2.39	Series Sealing			
7530	728	559	524	71	2.50	Series Sealing			
7550	716	548	512	79	2.54	Series Sealing			
7560	–	539	–	86	–			700<	
7570	440	363	342	80–95	5.42	Solder Glass	Ferrites	550	15
7572	370	–	–	90–100	–	Frit Kit	Pyroceran Bond Cement No. 95	450	
7574	645	–	–	40–50	–		Pyroceran Bond Cement No. 45	750	
7575	370	–	–	80–95	–		Pyroceran Bond Cement No. 89	450	
7578	445	–	–	60–75	–			525	
7583	370	–	–	70–90	–		Devitrifies at 450	485	18.9
7587	370	–	–	84	–		Devitrifies at 450	510	18.9
7588	370	–	–	80–90	–		Alumina & Beryllia	485	
7720	755	523	484	36	2.35	Borosilicate	W		
7750	–	473	–	40	–			700<	
8161	600	435	400	90			Ferrite Sealing Glass		
8407	662	576	550	100			Ferrite Sealing Glass		
8463	377	316	300	104	6.22	Lead Borate	Ferrite Sealing Glass		
8875	652	470	425	83			Ferrite Sealing Glass		
9013	656	462	423	89	2.63	Lead Free Sealing	Ferrite Sealing Glass		
9019	680	490	450	99	2.59	Lead Free Sealing	Ferrite Sealing Glass		
9776	337	289	–	125	6.95	Solder Glasses	Ferrite Sealing Glass		

literature sources. These include:

1) Table XV	Jenaer Glass works Schott (U.S. Branch release)
2) Tables XVI to XXIV	were reproduced from a German publication (R. Kleinteich).
3) Table XVI	Solder Glasses Jenaer Glasswerke Schott (German source)
4) Table XVII	Solder Glasses Glasswerke Wertheim a/Main
5) Table XVIII	Solder Glasses Glasswerke Ruhr Essen
6) Table XIX	Solder Glasses OSRAM
7) Table XX	Assorted German Manufactures
8) Table XXI	Assorted British Manufactures
9) Table XXII	Solder Glasses Philips Gloelampen Fabrik (Dutch)
10) Table XXIII	Solder Glass Glassworks de Baccaral (France)
11) Table XXIV	Solder Glasses Kavalier Works (CSSR)
12) Table XXV	Comp. Prop. of Neytrom Glasses (A. Danzin)
13) Table XXVI	Comp. and Prop. of Kavalier Glasses (W. Espe et. al.)
14) Table XXVII	Assorted European Solder Glasses (H. Kalsing)
15) Table XXVIII	Assorted European Solder Glass (E. Umblia)

TABLE X
Listing of Corning and Kimble glasses which are essentially equivalent.[12]

Kimble	Corning	Kimble	Corning
KG–1	0010	K–704	7040
KG–12	0120	K–705	7050
R–6	0080	ES–1	7070
EN–1	7052	IG–1	8870
EG–4	8871	IS–8	0211
K–772	7720	TH–10	0129
KG–33	7740	TL–2	9019
EK–3	0128	TM–5	9010
EN–3	3320	EZ–1	1720
ER–1	7761	N–51–A	7800

TABLE XI

Physical and chemical properties of sealing glasses† (Owens – Illinois. Recommended for electronics industry).

Type	Article Number	Volume Resistivity ρ (ohm-cm) Expressed as logarithim of ρ		Power Factor (Δ%) At 25°C and 1 mc	Dielectric Constant (At 25°C and 1 mc	Thermal Expansion Coefficient x 10^7 (0-300°C) (per °C)	Thermal Contraction Coefficient[1] x 10^7 (Annealing Point to 25°C) (per °C)	Chemical Durability [Average Weight loss of Fired Sealant] [30 minutes at 121°C] (mg/cm^2)		Density (gms/cc)
		250°C	350°C					H_2O	N/50 HCL	
V	**00130 [SG7]**	12.4	10.5	0.80	8.2	41	60	0.05	5.27	4.07
V	**00158 [SG67]**	11.1	8.9	0.15	12.5	83	102	0.62	3.10	5.38
	00331 [EN1]	9.0	7.2	0.26	5.1	47	62	NEGLIGIBLE		2.27
	00338 [IN3]	7.1	5.7	0.63	6.7	56	70	NEGLIGIBLE		2.32
	00560[5] [CV-101]	7.6	6.4	1.5	18.5	94	98	1.71	7.13	6.48
C	**00564[5] [CV97]**	7.8	6.4	1.3	23.8	83	89	2.33	6.66	6.3
C	**00578[5] [CV102]**	6.8	5.5	1.8	24.8	108	116	3.57	2.48	6.49
	00583[5] [CV432]	6.6	5.0	0.06	27.3	117	127	0.14	1.22	6.55
	00756 [CV98]	8.3	6.7	1.6	20.6	75	80	2.12	7.60	6.0
	00766 [CV135]	8.5	6.9	0.94	21.5	87	95	1.98	7.66	6.05

†Package sealants materials for microelectronics.

[1] For the crystallizing sealants, the contraction coefficient is measured from the recommended holding temperature to 25°C.

[2] The annealing point and the softening point apply only to the vitreous sealants.

[3] The time and temperature are interrelated. Seals can be made at shorter times by elevating the temperature.

[4] These sealants strongly absorb infrared radiation. Seals can be fabricated in less than one minute with the appropriate infrared source.

[5] These are basic materials that can either be used as supplied or modified by user. The materials to which the resulting product will seal will be determined by the properties of the modified sealant.

[6] These temperatures can be tolerated for up to 10 minutes.

V = vitreous
C = crystallizing

TABLE XI (*continued*)

Type	Article Number	Annealing Point[2] (°C)	Fiber Softening Point[2] (°C)	Recommended Sealing Cycle (Furnace Seals)		Maximum Reheat Temperature[6] (°C)	Sealable To	
				Temperature (°C)	Time (Minutes)		Glasses and Ceramics	Metals and Alloys
V	00130 [SG7]	469	571	615	45[3] [4]	550	EN-1 96% alumina	Iron-Nickel-Cobalt Alloy: ASTM #F-15 (e.g., Kovar,® Therlo,® Rodar.®) 42% Nickel-Iron Alloy: ASTM #F-30.
V	00158 [SG67]	365	441	470	20[3] [4]	425	KG-12, steatite, forsterite	Nickel-Chrome-Iron Alloy: ASTM #F-31 (e.g., Sylvania #4, Carpenter #426.) Dumet: ASTM #F-29. 52% Nickel-Iron Alloy: ASTM #F-30.
	00331 [EN1]	482	716	740	15[3]	700	96% alumina	Iron-Nickel-Cobalt Alloy: ASTM #F-15 (e.g., Kovar,® Therlo,® Rodar.®) 42% Nickel-Iron Alloy: ASTM #F-30.
	00338 [IN3]	521	710	735	15[3]	700	96% alumina	Iron-Nickel-Cobalt Alloy: ASTM #F-15 (e.g., Kovar,® Therlo,® Rodar.®) 44% & 46% Nickel-Iron Alloy: ASTM #F-30.
	00560[5] [CV-101]			425	60	525	KG-12, steatite, forsterite	Nickel-Chrome-Iron Alloy: ASTM #F-31 (e.g., Sylvania #4, Carpenter #426.) Dumet: ASTM #F-29. 52% Nickel-Iron Alloy: ASTM #F-30.
C	00564[5] [CV97]			460	60	525	KG-12, beryllia	Nickel-Chrome-Iron Alloy: ASTM #F-31 (e.g., Sylvania #4, Carpenter #426.) Dumet: ASTM #F-29. 49% & 52% Nickel-Iron Alloy: ASTM #F-30. Platinum Titanium
C	00578[5] [CV102]			380	60	510	TL-2 TH-10	18% Chrome-Iron Alloy: ASTM #F-256 (e.g., #430 Alloy.)
	00583[5] [CV432]			365	30	450		#302 Stainless Steel #304 Stainless Steel Iron
	00756 [CV98]			450	30	525	96% alumina	Iron-Nickel-Cobalt Alloy: ASTM #F-15 (e.g., Kovar,® Therlo,® Rodar.®) 44% & 46% Nickel-Iron Alloy: ASTM #F-30.
	00766 [CV135]			435	60	550	KG-12, steatite, beryllia, forsterite	Nickel-Chrome-Iron Alloy: ASTM #F-31 (e.g., Sylvania #4, Carpenter #426.) Dumet: ASTM #F-29. 52% Nickel-Iron Alloy: ASTM #F-30.

TABLE XII
Solder glasses (Kimble glass catalogue; Owens – Illinois).

SOLDER GLASS		Seal to Mat'l. of Therm. Exp. $\Delta L/L \times 10^{-7}/°C$ (0-300°C)	Sealing Temp. Range and Time	Density gm/cc	Anneal. Point °C	Fiber Soft. Point °C	Volume Resistivity (Log ρ ohm-cm)		Dielectric Properties (1 Mh 25°C)	
No.	Type						@ 250°C	@ 350°C	K	Δ%
SG-7	Vitreous	45 — 55	600°C — 60 min. under 625°C — 30 min. load.	4.07	469	571	12.4	10.5	8.2	0.80
SG-67	Vitreous	85 — 95	460°-480°C — 15-30 min. under load.	5.38	365	441	11.1	8.9	12.5	0.15
SG-68	Vitreous	95 — 105	440°-460°C — 30-60 min. under load.	5.90	348	412	10.3	8.3	14.8	0.16
CV-9	Cryst.	110 — 120	435°-455°C — 60 min.	6.51	308	374	8.1	6.7	20.2	0.59
CV-97	Cryst.	75 — 90	450°-460°C — 60-75 min.	6.30	325	394	7.8	6.4	23.8	1.3
CV-98	Cryst.	70 — 85	440°-460°C — 60 min.	- - -	- - -	- - -	8.3	6.7	20.6	1.6
CV-101	Cryst.	90 — 100	415°-450°C — 60 min.	6.48	309	372	7.6	6.4	18.5	1.5
CV-102	Cryst.	100 — 120	375°-385°C — 60 min.	6.49	- - -	346	6.8	5.5	24.8	1.8
CV-130	Cryst.	90 — 100	440°-460°C — 60 min.	6.53	305	375	7.3	6.0	25.0	2.0
ECV-1014 (CV-133)	Cryst.	90 — 100	425°-435°C — 60 min.	6.25	- - -	- - -	8.6	6.9	22.8	0.89
CV-135	Cryst.	85 — 95	420°-430°C — 60 min.	6.05	- - -	- - -	8.5	6.9	21.5	0.94
CV-137	Cryst.	90 — 100	420°-450°C — 60 min.	6.53	306	372	7.4	6.2	18.0	1.7
CV-285	Cryst.	50 — 70	630°-650°C — 60 min.	4.09	486	579	13.8	11.2	8.4	0.14
CV-432	Cryst.	110 — 125	360°-370°C — 30 min.	6.55	- - -	330	6.6	5.0	27.3	0.059
CV-635	Cryst.	35 — 45	680°-700°C — 60 min.	3.90	530	632	12.8	11.0	7.0	0.08
CC-10	Conduct. Cryst.	90 — 105	415°-435°C — 60 min.	6.48	- - -	- - -	.006*	.006*	- - -	- - -
CC-11	Conduct. Cryst.	94 — 105	415°-435°C — 60 min.	6.47	- - -	- - -	.003*	.003*	- - -	- - -

†These values in ohm-cm at room temperature.

TABLE XIII
Kimble solder glasses – physical properties.

SOLDER GLASS NO.	SG-7	SG-67	SG-68	CV-9	CV-97	CV-98	CV-101
Firing Temperature	625°C	460°C	440°C	445°C	450°C	450°C	425°C
Annealing Point	469°C	365°C	348°C	–	–	–	–
Expansion Coefficient (0°-300°C) x 10^{-7}/°C	41	83	90	112	83	76	94
Contraction Coefficient (A.P.–25°C) or (F.T.*–25°C)	60	102	115	121	89	80	98
Vitreous Contraction Coefficient (A.P.–15°C)–25°C x 10^{-7}/°C	53	94	104	–	–	–	–
Crystallizing Contraction Coefficient (F.T.*–25°C) x 10^{-7}/°C	–	–	–	121	89	80	98
Materials recommended for sealing with the Solder Glass at the indicated temperature and their contraction coefficients calculated at the same temperature	N-51A (51) EN-1 (54) K-650 (52) KOVAR (51)	TM-5 (92) KG-12 (92) KG-1 (95) R-6 (96) No. 4 ALLOY (89)	TH-10 (100) TL-2 (101) No.430 ALLOY (110)	EU-3 (136)	RP-3 (82) A-3004 (87) No. 4 ALLOY (106)	RP-3 (82) A-3004 (87)	TM-5 (99) KG-12 (99) R-6 (99) KG-1 (105) TH-10 (105) TL-2 (106) No. 4 ALLOY (102)

Firing Temperature

TABLE XIII (*continued*)

CV-102	CV-130	ECV-1014 (CV-133)	CV-135	CV-137	CV-285	CV-432	CV-635	CC-10	CC-11
375°C	450°C	430°C	425°C	425°C	640°C	365°C	690°C	425°C	425°C
–	–	–	–	–	–	–	–	–	–
108	95	92	87	95	51	117	32	99	103
116	101	100	95	100	70	127	48	104	108
–	–	–	–	–	–	–	–	–	–
116	101	100	95	100	70	127	48	104	108
EU-3 (125) No. 4 ALLOY (111)	R-6 (101) TM-5 (105) KG-12 (105) TH-10 (108) TL-2 (109) No. 4 ALLOY (106) No. 430 ALLOY (112)	R-6 (100) TM-5 (101) KG-12 (101) KG-1 (106) TH-10 (106) TL-2 (107) No. 4 ALLOY (103) No. 430 ALLOY (111)	TM-5 (99) KG-12 (99) R-6 (99) No. 4 ALLOY (102)	TM-5 (99) KG-12 (99) R-6 (99) KG-1 (105) TH-10 (105) TL 2 (106) No. 4 ALLOY (102)	ALUMINA (50-70) BERYLLIA (≈72)	EU-3 (116)	EE-2 (50)	TM-5 (99) KG-12 (99) R-6 (99) KG-1 (105) TH-10 (105) TL-2 (106) No. 4 ALLOY (102) No. 430 ALLOY (111)	KG-1 (105) TH-10 (105) TL-2 (106) No. 4 ALLOY (102) No. 430 ALLOY (111)

TABLE XIV
General Electric sealing glasses.†

Code	Designation	Principal Use	Linear Thermal Expansion $0–350^{\circ}$ α 10^7	Density	Viscosity Data (°C)			
					Strain Point	Anneal Point	Softening Point	Refractive Index
138	Potash Barium Lead	Color TV Necks	95	3.17	445	485	665	1.580
199	Potash Soda Lead	Iron Sealing	120	3.25	350	380	535	1.590
774	Borosilicate	General	32	2.23	505	560	815	1.474
974	Borosilicate	UV Transm	50	2.19	440	480	720	1.474
†"Glass in the 20th Century for Industyr and Research", Lamp Glass Department, General Electric Co.								
GSC1			13.9					
GSC3			14.5					
GSC4			24.1					

TABLE XV

Physical and chemical properties of industrial glasses (Excerpt from Brochure No. 2051/1E, Jenaer Glasswerke Schott).

Solder Glasses

Glass No.†)	Glass type	For soldering of materials with	Soldering temperature after 1 hr soldering time ¹)	Linear expansion coefficient	Transformation temperature	Temperature at viscosities (poises) of			Density	tk 100	K	tan δ · 10^4
		$\alpha \cdot 10^7$		$\alpha \cdot 10^7$ (20—300 °C)	Tg	$10^{7.6}$	10^5	10^4			at 1 Mcps and 20°C	
		1/°C	°C	1/°C	°C	°C			g/cm³	°C		
8462	Alumo-boro-silicate glass	60 — 70	650	55	429	565	660	737	2.31	350	5.4	16.5
8465	Lead borate glass	85 — 95	520	82	385	461	525	566	5.38	375	14.9	27
8467	Lead borate glass	90 — 105	490	91	354	418	487	518	5.69	361	15.4	29
8468	Lead borate glass	95 — 110	450	96	340	405	425	460	5.98	333	16.3	31
8470	Free from lead borate oxide	105 — 115	680	100	439	570	680	748	2.84	295	7.7	15.5
8471	Lead borate glass	110 — 125	440	106	332	389	427	456	6.23	330	17	32
8472	Lead borate glass	125 — 140	410	120	298	360	400	426	6.75	281	18.2	31
8474	Alkali phosphate glass	~ 200	480	190	326	420	473	512	2.56	173	7.5	27

†Reference to previous types: No. 8462 identical with 8435
8465 supersedes 8461 and earlier 8462
8467 supersedes 8461
8470 identical with 8463
8472 supersedes earlier 8468[2])

[1] Approximate values for unimpeded smooth flowing of solders on glass surfaces.

[2] Previous type No. 8468 is crystallized during soldering; is listed with new No. 8587.

Remarks concerning columns, see main table (inside).

Glass type No.	Suitable for sealing to	$\alpha \cdot 10^7$ 1/°C (20 — 300 °C)	Tg	Temperature of glass in °C at viscosities (poises) of				d	tk 100
			°C	$10^{14.5}$	$10^{13.0}$	$10^{7.6}$	10^4	g/cm³	°C
8436	Sapphire, Vacon 70	67	620	595	630	810	1095	2.72	—
8447	2877 — Vacon 10	48	465	437	492	720	1030	2.26	264
8448	8330 — 8487	38	550	—	560	807	1205	2.29	235
8449	8486 — 2877	45	520	505	552	780	1150	2.29	330
8450	2877 — KER 220, 2954	54	568	—	575	778	1130	2.44	200
8454	KER 221 — Vacon 70	64	565	540	575	745	1050	2.49	225

Remarks concerning column 2: Type designation of ceramics is in accordance with German standard DIN 40 685;
Manufacturer of Vacon metal alloys: Vakuumschmelze Hanau (West Germany).

Remarks concerning columns, see main table (inside).

TABLE XVI
Solder glass of Jenaer Glasswork Schott & Gen., Mainz.[23]

Code Glass No.	Glass Type	Coefficient of Thermal Expan. α $(10^{-7}/{}^{\circ}C)$		Tg °C	T_{soft} °C	Sealable To
		0–100° C	20–300° C			
8330	Duran 50	32	32	530	815	Tungsten
2955	Supremax	33	37	715	938	Tungsten
8409	Supremax 56	37	41	745	960	Tungsten
3891	Suprax	39	40	553	793	Tungsten
8212	Wolframglas	40	41	495	742	Tungsten
1646	Wolframglas	41	42	515	754	Tungsten
8447	Mo-Glas & for Fe-Ni-Co-Leg.	47	48	465	720	Moly u. Fe-Ni-Co-Alloys
2877	Geräteglas G 20	48	49	560	794	Moly
8412	Fiolax, klar	48	49	558	783	
1639	Mo-Glass	49	50	531	736	Moly
8243	Mo-Glass and for	50	52	485	715	Moly, Vacon 10
1447	Fe-Ni-Co-Leg.	50	51	528	725	Moly, Vacon 12, Kovar, Cu
2954	Thermometerglass	60	64	590	780	Vacon 20, Kovar
16 III	Normalglass	82	90	543	712	Pt, Cu-Sleeve, Vacovit 501 and 511
8196	FS-Kolbenglass	86	94	437	660	Pt, Vacovit 485 and 426
8095	Bleiglass	88	95	425	628	Pd, Pt and Pt-Cu-Sleeve Vacovit 485 and 426
8405	Uviolglass	92	97	440	657	Pt, Pt-Cu, Vacovit 485 u. 426
4210	Eisenglass	116	127	445	614	Iron

TABLE XVII
Solder glasses of Glaswerk Wertheim, Wertheim am Main.[23]

Glass Type		CTE $\propto(10^{-7}/^{o}C)$		Tg ^{o}C	T_{soft} ^{o}C	Sealable To
		20–100° C	20–400° C			
Mo-Glass	EW	42	44	505	565	Moly, Kovar
Resistenzglass	R	57	63	570	620	Vacon 10, 12, 20
Geräteglass	S	72	81	530	590	
Normalglass	NW	80	89	540	600	Pt, Pt-Cu-Sleeve, Vacovit 501
Geräteglass	GW	87	~ 95	525	580	Pt, Pt-Cu-Sleeve, Vacovit 501, 511
Einschmelzglass	KW	86	102	545	595	Pt, Pt-Cu-Sleeve, Vacovit 511, 540
Einschmelzglass	LW	88	97	520	570	Pt, Pt-Cu-Sleeve, Vacovit 426, 511,540
Leuchtröhrenglass		88	97	500	550	
Einschmelzglass	MW	89	99	420	460	Pt, Pt-Cu-Sleeve, Vacovit 426
Apparateglass	AW	90	100	505	570	Pt, Pt-Sleeve, Pd

TABLE XVIII
Solder glasses, Glaswerke Ruhr, Essen.[23]

	CTE $\propto(10^{-7}/^{o}C)$		Tg ^{o}C	T_{soft} ^{o}C	Sealable To
	0–100° C	20–300° C			
AR-Glass	91	95	520	~718	Pt, Pt-Sleeve, Vacovit 501
ARN-Glass	~ 78	~ 80	525	~720	Pt, Pt-Cu-Sleeve
LR-weiss	107	110	479	~ 660	Pt, Pd, Pt-Sleeve, Vacovit 025
LR-braun	106	109	492	~671	
MGR-Glass	101	105	484	~671	Pt, Pt-Cu-Sleeve, Pd, Vacovit 426

TABLE XIX
Solder glasses Osram GMBH. Munchen/Augsburg.[23]

Glass Type	CTE $\propto(10^{-7}/^{o}C)$		Tg ^{o}C	T_{soft} ^{o}C	Seal To
	0–150° C	0–300° C			
Tube Glass 905c	91	102	500	740	Pt, Pt-Sleeve, Vacovit 501
Solder Glass 123a	88	97	415	682	Pt;Cu-Sleeve, Vacovit 501
Solder Glass 301b	91	96	460	688	Pt, Pt-Cu-Sleeve, Vacovit 501
Solder Glass 911b	49	53	500	752	Mo, Kovar, Vacon 12
Solder Glass 919c	50	54	500	744	Mo, Kovar, Vacon 12 und 10
Solder Glass 906c	45	49	508	770	Molybdenum
Solder Glass 362a	41	42	480	820	Tungsten

TABLE XX

Assorted other German manufactures.[23]

Glass Type	CTE $\propto(10^{-7}/{}^{\circ}C)$		Tg ° C	T_{soft} ° C	Manufact.	Seal To
	20–100° C	20–300° C				
Silibor	8		1000		S	Sealing Glass
Rasotherm Glass	31	33	554	621	S	Tungsten
Wolframe Glass 1646 III	41	45	540	600	S	Tungsten
Apparatus Glass	46	48	558	608	S	Molybdenum
Molybd Glass 1639 III	46	48	532	570	S	Molybdenum, Vacon 10
Molyb Glass 1447 III	50	55	533	570	S	Molybdenum, Vacon 12
Therm-Glass 2954 III	58	65	593	629	S	Kovar, Vacon
Normal Glass 16 III	80	84	550	589	S	Pt, Pt-Cu-Sleeve, Vacovit 511
Solder Glass 3079 III	81	94	481	525	S	Pt, Pt-Cu-Sleeve
Platinun Glass 2962 III	80	90	518	560	S	Pt, Pt-Sleeve, Pd, Vacovit 501, 511
Fisher-prima	85	92	518	547	F	Pt, Pt-Cu-Sleeve, Vacovit 501
Gege-Eff	76	84	535	581	F	Pt-Cu-Sleeve, Vacovit 501
Iron Glass	109	125	474	520	F	Pure Iron
Special Glass 357	67		544	593	F	Kovar
X-Glass	95	103	503	540	F	Cu-Ring und Pd
Molybd Glass 637a	46	47	587	630	O	Molybdenum
Glass 362a	39	40	553	592	O	Tungsten
A-Glass	67	70	568	610	J	
Lead Glass	87	96	443	484	J	Pt-Cu-Sleeve
N-Glass	82	90	537	578	J	Pt, Pt-Cu-Sleeve, Vacovit 501

Manufactures

S = Saale-Glas GmbH, Jena.
F = VEB Glaswerk Gustav Fischer, Ilmenau.
O = VEB Osram, Weisswasser.
J = VEB Westglaswerke, Ilmenau.

TABLE XXI
British solder glasses.[23]

Glass Code	CTE $(10^{-7}/^{\circ}C)$ 0–300° C	T_{an} °C	T_{soft} °C	Manufact.	Seal To
Dial 36	36	580		PT	Tungsten
Bluesil	37	570		PT	Tungsten
Kodial	49	535		PT	Moly, Kovar
Normal	84	560		PT	Ni-Fe-Alloy
Dial 444	88	510		PT	Pt, Pt-Cu-Sleeve
Neon Soda	96	520		PT	Pt, Pt-Sleeve, Fe-Cr-Alloy
C 9	36	525	775	BT	Tungsten
C 11	45	575	795	BT	Moly
C 46	43	775	840	BT	Moly
C 40	48	505	710	BT	Kovar, Vacon
C 41	128	540	620	BT	Iron
C 12	90	435	630	BT	Pt, Pt-Sleeve, Ni-Fe-Alloy
GH 1 Hysil	35	556	780	CH	Tungsten
GS 1 Intasil	38	600		CH	Tungsten
GS 4	44	610		CH	Moly
GSB	52	450	715	CH	Kovar, Nilo
GWB	100	400	610	CH	Pt, Pt-Sleeve, Fe-Cr-Alloy
FCN	48	480	680	GE	Kovar, Nilo
W 1	37	580	760	GE	Tungsten
HH	46	590	780	GE	Moly
M 6	73	580	600	GE	
L 1	90	430	610	GE	Pt, Pt-Cu-Moly,Ni-Fe-Alloy

Manufactures
PT = Plowden & Thompson Limited, Stourbridge
BT = British Tomson, Houston
CH = Chance Brothers
GE = Gen. Electric Co, Wembley

TABLE XXII
Dutch solder glasses Philips-Gloelampen Fabrik.[23]

Glass Code	CTE $\alpha(10^{-7}/^{\circ}C)$ 0–300° C	T_{an} °C	T_{soft} °C	Seal To
08	39	550	770	Tungsten
18	38	740	955	Tungsten
28	48	495	720	Moly, Kovar
158	50	515	706	Moly, Kovar
01	92	425	620	Pt, Pt-Sleeve Ni-Fe-Alloy
143	96,5	485	685	Pt, Pt-Sleeve Ni-Fe- Alloy

TABLE XXIII
French solder glass of Cristallerie de Baccaral.[23]

Glass Code	CTE $\alpha\ (10^{-7}/^{\circ}C)$ 20–100° C	Tg °C	Seal To
E- Neutrohm	49	510	Moly, Kovar
T- Neutrohm	35	540	Tungsten
P- Neutrohm	50	560	Moly

TABLE XXIV
Czechoslovak solder glass of Kavalier-Glaswerke.[23]

Glass Code	CTE $\alpha(10^{-7}/^{\circ}C)$	Tg °C	T_{defor} °C	Seal To
Wolframglas	40	483	575	Tungsten
WoKa				
Kovarglas K705	47	465	540	Kovar, Moly
Moly	50	550	605	Moly
MoKa				
D 47	87	530	560	N-Fe-Alloy
SIMAX	31	490	590	Tungsten
LL (K707)	32	480	575	Tungsten

TABLE XXV
Composition and properties of Neutrohm Glass.[23]

	Neutrohm T	Neutrohm E	Neutrohm P
SiO_2	52,4	50	54
Na_2O	0,7	1,8	0,7
Al_2O_3	5	5	5
MgO	1	1	1
ZnO	2,5	1	2,5
PbO	29	28,7	12
BaO	–	–	10,5
B_2O_3	8,5	12	8
As_2O_3	0,6	0,5	0,5
CaO	–	–	6
T_{an}, °C	540	510	560
T_K 100	355	322	340
Solubility Index (German Powder Method)	8 mg	8 mg	–

TABLE XXVI
Composition and properties of Czechslovak solder glasses.[80]

Comp. Wt %	Glass Type			
	K 707	WoKa	MoKa	K 705
SiO_2	72,8	70	75	66
B_2O_3	22,3	14,5	10	21
PbO		5,5		
Al_2O_3	1,1	4,8	4,9	4,8
Na_2O	1,5	1,3	7,2	3
K_2O	1,2	3,2	1,3	4
CaO	0,8	1,8	1,6	
Li_2O	0,2			
As_2O_3	Trace			
F				
Cl				
CTE α(20–300° C)	$33{,}4\cdot10^{-7}$	$40\cdot10^{-7}$	$50\cdot10^{-7}$	$47\cdot10^{-7}$

TABLE XXVII

Some European solder glasses.[84]

Code	Manufacturer	Glass Seals to Metals	Coeff. of Expansion With $\alpha .10^7/^oC$	SiO_2	P_2O_5	B_2O_3	Al_2O_3	Na_2O	K_2O	MgO	CaO	Sb_2O_5	BaO	PbO
	TH	Cu	142		33.5	7.0	15.5	14.0	—	—	—	—	—	30.0
1075	N	Fe–Ni	53	31	—	28	7	2	—	—	—	—	—	29
L1	GE	Pt	—	56.6	—	—	0.8	5.1	7.2	—	—	—	—	30.2
C12	TH	Pt	—	57.4	—	—	1.3	3.9	7.6	—	—	—	—	29.3
FCN	GE	Fe–Ni–Co	50	66	—	24.5	1.9	4.3	3	—	0.4	—	—	—
184	N	Fe–Ni–Co	50	65	—	23	5	7	—	—	—	—	—	—
96/2	SOG	Fe–Ni–Co	50	70.60	—	11.75	4.66	10.70	1.66	0.10	0.36	—	—	—
C40	TH	Kovar	47	65.9	—	24.0	1.8	3.8	4.2	—	—	—	—	—
GS3	CH	Kovar	47	67	—	21	4	3	4.5	—	—	0.4	—	—
	H	Kovar	47	66	—	24	2	8	8	—	—	—	—	—
L14	GE	Cr–Fe	—	53	—	—	0.8	3.8	10.3	—	31	—	—	29.7
286	N	Cr–Fe	—	54	—	—	—	5	8	—	—	—	4	29
C31	TH	Cr–Fe	—	52	—	—	1.0	—	14.5	—	2.5	—	—	30.0
	SFRE	Cr–Fe	—	55.0	—	—	—	3.9	8.7	—	4.0	—	8.2	20.0
											Together at Least 29%			

TH.	Thompson–Houston Co.
N	Navias
GE	General Electric Ltd. (Wembley)
SOG	Sendlinger Optische Glas Werke
CH	Chance Brothers
H	Helander
SFRE	Société Fraçais Radio Eléctrique.

TABLE XVIII
European solder glass.[5 6]

Manufact.	Glass Code							CTE	T_{soft}	T_{work}
		SiO_2	B_2O_3	Al_2O_3	Na_2O	PbO	ZnO	$\alpha \times 10^{-6}$		
BTH	P2	0,3	20,6			79,4		9,5		370
BTH	PZ7	6,3	21,5			72,5		8,6		380
BTH	PZ13	0,9	12,5		15,0	71,5		9,2		380
BTH	Soft solder Glass	>5	?	?	?	70	?	8,3	$T_d = 410$	>500
BTH	PZS2	6	14,7			63,8	16,6	7,6	415	550
GEC, Wembley	GSS 38		20			80	2,5	9,6	$T_t = 300$	475
GEC, Wembley	GSS 1	2,0	16			84	8,0	9,2	325	500
GEC, Wembley	GSS 34	2,5	30			70		8,0	360	525
Verrieries de Bagmeaux	G 50								354	550
Verrieries de Bagmeaux	M 130							11,1	360	560
Verrieries de Bagmeaux	M 129							9,0	420	620
Philips	Lödglas		16			80	4	9,6	$T_d = 420$	
Schott & Gen.	8468		+			+	++	12,4	$T_t = 265$	350
Mainz	8461	+	+			+		8,3	403	>500
Mainz	8435	+	+	+	Li +	+		5,8	412	>600
Fischer, Ilmenau	F 3	14,3	11,2	0,2	0,5	74,0		9,0	$T_d \approx 400$	ca 550
Telefunken	VUS	2,9	12,1			77,2	7,8	9,1	$T_t = 340$	
Telefunken	T 209	5	14,8	1	1,2	78		9,0	365	
Telefunken	Solder Glass for Hard Glass	7	59	1		30	3	5–6		650–700
Telefunken		10	50	P_2O_5:2		35	3			
Telefunken		15	45	1		38	1			
VEB, Weisswasser	Solder glass	6,6	20,4			73		7,8		500
VUS, Hradec	8083	?	7,5	?	?	85	?	10,2	$T_d = 225$	
Králové (CSR)	7941		12,5			79,5	8,0	9,5	318	
Králové (CSR)	7980	2,9	12,1			72,2	7,8	9,1	340	
Králové (CSR)	7966		17,5			72,5	10,0	8,1	340	
Králové (CSR)	7908		16,0			80,0	4,0	9,1	360	
Králové (CSR)	8009	4,8	11,9			78,6	4,8	8,6	365	
Králové (CSR)	7909		20,0			76,0	4,0	8,1	400	

T_d = deformation temperature; T_t = transformation temperature; T_m = Softening temperature

3. SURVEY OF THE PATENT LITERATURE ON SOLDER GLASSES

This is essentially a bibliography of foreign and domestic patents.

The patents are organized according to coefficient of expansions. The main constituents and other properties as far as possible are listed briefly. It should be pointed out that the physical properties as listed in the patents are far from complete. Only those properties which are relevant to the invention are listed. Special sealing glasses as well as patents pertaining to glass sealing processes are each listed separately with appropriate comments. Number, country of origin, year of release, inventor and assignors are listed, the latter if available.

CTE $< 40 \times 10^{-7}/^\circ C$

U.S 3404015 (1968) Dumbugh, W. H. (C)
3459569 (1969) Ellis, J. L. (O–I)
3564587 (1971) Ellis, J. L. (O–I)
German 2112366 (1971) Baak, N. T. (O–I)
French 1524470 (1968) Borgrave

Devitrifying Glasses

U.S. 2920971 (1960) Stookey, S. D. (C)
This is the well known "Pyroceram."
Major constituents: $SiO_2 > 40\%$, $Al_2O_3 > 10\%$
Minor constituents: Alkalies, ZnO, Cu_2O, PbO, ZrO_2, TiO_2, alkaline earth metals.

CTE 39 to 42 $\times 10^{-7}/^\circ C$

Suitable for sealing to tungsten.

U.S. 2695241 (1954) Calis, J. (Comp. Gen. de Telegraph, sans fil)
2933552 (1960) Schurecht, H. E. (Champion Spark plug)
3408222 (1968) Navias, L. (GE)
3469729 (1969) Grekila, R. R. (WE)
German 1046204 (1958) Dallenbach, W. (FKG FRITZ KESSELRING)
2000412 (1970) Wallis, G. (Mallory)
German 48342 (1966) Hinz, W.

These glasses are essentially a) Aluminum borosilicates: SiO_2 30–80%, B_2O_3 0–20%, Al_2O_3 0–60%, CaO 0–55%, plus various modifiers usually < 1% or b) High Lead Glasses: PbO 60–75%, $Al_2O_3 \sim 10\%$, $B_2O_3 \sim 10\%$. Sealing temperature for most of these glasses is ~ 700°C.

CTE 45 to 51 $\times 10^{-7}/^\circ C$

Suitable for sealing to molybdenum

U.S. 3088834 (1963) Pirooz, P. P. (O–I)
3088835 (1963) Pirooz, P. P. (O–I)
3113878 (1963) Martin, F. W. (C)
3467509 (1969) Foster, L. C. (Zenith)
3503763 (1970) Mills, W. H. (Anchor-Hockin
French 1451857 (1966) Bristow, R. H. (GE)

These are mostly lead-zinc borates glasses, PbO 0 to 25%, B_2O_3 4 to 25%, Al_2O_3 0 to 20%, SiO_2 10 to 50%, ZnO 50 to 70% containing devitrification agents (TiO_2, ZrO_2) and modifiers. The softening temperatures of these glasses are reported to be between ~ 600 and 700°C. Devitrification temperatures > 700°C where applicable.

CTE 48 to 62 $\times 10^{-7}/^\circ C$

Suitable for sealing to Kovar

U.S. 2693423 (1959) Rogers, F. R.
3088833 (1963) Pirooz, P. P. (O–I)
3303399 (1967) Hoogendoorn, H. M. (IBM)
3331731 (1967) Baar, N. T. (O–I)
3420684 (1969) Hagendorn, E. C. (O–I)
3420685 (1969) Martin, F. (C)
3493405 (1970) Thomas, G. L. (GE)
French 1447732 (1966) Smith, T. P. (C)
2018851 (1970) (Jena)
German 1012440 (1957) Sack, W. (Jena)
1078293 (1960) Ruschke, H. (GE, British)
British 723087 (1955) (Thomson–Houston)
884004 (1955) (GE, British)
1209869 (1970) Shipton, G. O. (O–I)

These glasses are mostly Pb–Zn, Al, borosilicates. SiO_2 0 to 70%, Al_2O_3 0 to 20%, ZnO 0 to 60%, B_2O_3 0 to 50%, PbO 0 to 42% with appropriate modifiers up to 15% per oxide; or zinc vanadate glasses: V_2O_5 5 to 30%, ZnO 40 to 60%, B_2O_3 20 to 40%, SiO_2 0 to 10%, Al_2O_3 0 to 10% PbO 0 to 5%. The softening temperature ranges from ~450 to 800°C.

CTE $\cong$ *85 to 105* $\times 10^{-7}/^\circ C$

Suitable for sealing to alloys containing Fe–Ni–Cr

U.S. 2743553 (1956) Armistead, W. H. (C)
2770923 (1956) Dalton, R. H. (C)
2889952 (1959) Claypool, St. A. (C)
3061664 (1962) Kegg, R. R. (Kimberly)
3473999 (1969) Muchow, G. M. (O–I)
3486871 (1969) Martin, F. W. (C)
3534209 (1970) Anderson, R. C. H. (GE)
Netherlands 6513920 (1966)
Japan 6264 (1962) Yokota, R. (Toshiba)
U.S.S.R. 313789 (1969) Yalanskaya, V. A.

These glasses are either high $SiO_2 > 40\%$ and low $PbO \sim 20\%$ or low SiO_2 <5 % and high PbO > 60% containing Al_2O_3 0 to 10% and B_2O_3 0 to 22% with alkalis from 0 to 10% with other modifiers up to 10%. One of the glasses in this group is zinc-vanadates. Softening points range from 400 to 700°C. Most of these glasses readily devitrify at temperatures < 700°C.

CTE ≅ 91 to 100 x *10^{-7}/°C*

Suitable for sealing to copper and platinum

U.S.	2899575	(1959)	Vincent, H. B.	(O–I)
	2931142	(1960)	Veres, F.	(O–I)
	3075860	(1963)	Veres, F.	(O–I)
	3127278	(1964)	Francl, J.	(O–I)
	3312556	(1967)	Oikawa, M.	(Hitachi)
	3414465	(1968)	Baak, N. T.	(O–I)
	3454408	(1969)	Busdiecker, R. A.	(O–I)
French	1498179	(1967)	Pither, L. F.	(O–I)

Glasses in this group are either:

a) High PbO > 70% with additions of Al_2O_3, B_2O_3 and ZnO plus small amounts of modifiers or

b) Low PbO 0 to 50% with SiO_2 0–90% plus additions of V_2O_5, P_2O_5 and minor amounts of alkali and alkaline earth as well as transition and refractory metal oxides. The softening temperatures range from 300 to 800°C. The lead vanadates and zinc-lead borates devitrify readily.

CTE ≅ 110 to 130 x *10^{-7}/°C*

Suitable for sealing to iron

U.S.	2949376	(1960)	Comer, R. L.	(GMC)
	3240661	(1966)	Babcock, C. L.	(O–I)
	3407091	(1968)	Busdiecker, R. A.	(O–I)
	3408212	(1969)	Dumesnil, M. E.	(Fairch.)
	3480566	(1969)	Hoffman, L. C.	(DuPont)
	3485648	(1969)	Bishop, F. L.	(O–I)
French	1449425	(1966)		(Japan Electric Co.)

These glasses fall into many compositional categories such as aluminoborosilicates, vanadates, plumbates and aluminophosphates, with a large variety of modifiers. Their softening temperature is below 400°C, usually between 200 to 300°C. One glass devitrified at 350°C.

CTE > 130 x *10^{-7}/°C*

Suitable for sealing to iron

U.S.	2929727	(1960)	Oldenfield, L. F.	(GE, British)
	2937100	(1960)	Oldenfield, L. F.	(GE, British)
	2948992	(1960)	Oldenfield, L. F.	(GE British)
	3203715	(1965)	Benbenek, J. E.	(RCA)
	3449203	(1969)	Fisher, H. G.	(O–I)

These glasses are aluminosilicates or aluminium borosilicates containing conventional modifier alkalies 0–30%, alkaline earth oxides 0–10% and devitrifiers 0–30%. The softening temperatures in the range of 500–600°C.

Special Solder Glasses

Non-oxide glasses These glasses melt in the range of 100 to 400°C but have CTE's over 200 x 10^{-7}/°C. These are non-oxide glasses usually ternaries based on the elements S, Se, As, T1, I and Pb:

U.S.	3144318	(1964)	Bruen, Ch. P.	(Allied Chemical)
	3413187	(1968)	Krause, J. T.	(BTL)

Conducting and magnetic glasses This is a lead borate glass (PbO 60%, B_2O_3 10 to 20%) containing SiO_2 and Al_2O_3 plus Group II oxides in small amounts. Ag (or Cu) plus Ag_2O not only assures electrical conductivity but reduces devitrification tendencies. A similar basic glass is used loaded (up to 35% by wt.) with small particles (< 3μ diam.) to render it magnetic.

U.S.	3080328	(1963)	Billian, C. J.	(O–I)
	3249466	(1966)	Lusher, K. G.	(O–I)

Resealable solder glass A glass system was developed for repeatedly separating and resealing the same joint by mixing (75% to 25%) a devitrifying and non-devitrifying glass. Both glasses belong to the PbO–ZnO–B_2O_3 system with small amounts of SiO_2, BaO and CuO added. This glass has a work temperature of 440 to 532°C but devitrifies above that range.

U.S.	3291586	(1966)	Chapman, G. C.	(O–I)

Glass Sealing Processes

This section lists a number of patents describing various techniques of forming glass-to-metal or glass-to-glass seals.

Metal seals Both parts to be joined are coated by evaporation or sputtering with a layer of an appropriate metal. The seal then is formed either by a conventional solder technique using metal solders or low melting alloys, or by hot or cold pressing.

U.S.	2918757 (1959)	Frackl, J.	(O–I)
	306069 (1961)	Rhodas, J. L.	(RCA)
	3415556 (1968)	Reed, L.	(Varian)
	3481638 (1969)	Reed, L.	(Varian)
	3546363 (1970)	Pryors, J.	(Olin Mat.)
British	834972 (1960)		(English Ind.)
	940971 (1963)		(Philips, Neth.)
French	1551426 (1968)	Pryor, M. J.	(Olin Mat.)
German	2018752 (1970)	Klomp, J. T.	

Metal foil seal A suitable metal foil (i.e., Al) is interposed between the two parts (i.e., Sodalime and sapphire) and the parts are heated and or pressed together.

U.S.	2876596 (1959)	Kessler, S. W.	(RCA)
	3424568 (1969)	Martin, F. W.	(C)

Glazing techniques In this category the metal part is oxidized appropriately or one or both parts of the work piece are coated with a suitable film of glass or enamel. The seal then is formed by a variety of techniques such as heating under pressure or in a vacuum.

U.S.	2422215 (1942)	Amberg, Ch. R.	
	2717475 (1955)	McCarthy, H. J.	(Bomac)
	2819561 (1958)	Henry, K. M.	(O–I)
	2919210 (1959)	Steierman, B. L.	(O–I)
	3107757 (1963)	Breadner, R. L.	(GE, British)
	3171771 (1965)	Badger, A. E.	(Li–O–Ford)
	3222152 (1965)	Upton, L. O.	(Am. Opt.)
	3571487 (1971)	Tietze, A.	

In situ thickness measurements To measure the thickness of a glass-to-glass seal (or glass-to-metal seal), coloring agents in the solder glass are employed and optical absorption measurements are made after the seal is formed.

Germany (East)	72876 (1970)

ACKNOWLEDGMENT

The author acknowledges his indebtedness to the IBM System Products Division, East Fishkill library, especially Mrs. K. A. Murley for her assistance in the search, and to P. R. Langston R. R. Tummala and M. N. Turetzky for advice and many helpful discussions and revisions.

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