

PATENT SPECIFICATION

(11) 1339 640

NO DRAWINGS

1339 640

- (21) Application No. 60370/71 (22) Filed 29 Dec. 1971
 (31) Convention Application No. 102886 (32) Filed 30 Dec. 1970 in
 (33) United States of America (US)
 (44) Complete Specification published 5 Dec. 1973
 (51) International Classification C03C 3/30 3/22//C04B 37/04
 (52) Index at acceptance



C1M 11B3 11C1 11C4 11C5 11C7 11C9 11F14 11F15
 11F28 11F33 11F4 11F5 11F8 11J1 11K1 19B1
 7C6 7E1 7E11 7E12 7F19 7F20 D21 D22 D27
 D31A S19

(54) SEALANT GLASS

(71) We, OWENS-ILLINOIS, INC.,
 a corporation organised and existing under
 the laws of the State of Ohio, United States
 of America, of Toledo, State of Ohio, United
 States of America, (assignee of JOSEF
 FRANCEL, LESTER CORNELIUS MIN-
 NEMAN and NEIL BRIAN NOFZIGER),
 do hereby declare the invention, for which
 we pray that a patent may be granted to
 us, and the method by which it is to be
 performed, to be particularly described in and
 by the following statement:—

This invention relates to sealing glass com-
 positions and methods of using same. More
 particularly, this invention relates to sealing
 glass compositions particularly useful for
 bonding ceramic components in microelec-
 tronic circuitry.

Generally speaking, this invention repre-
 sents an improvement upon U.S. Patent No.
 3,250,631, the disclosure of which is incor-
 porated herein by reference.

It has long been known that sealing or
 solder glasses are advantageous means for
 sealing together pieces of material such as
 glass, ceramic, metal or the like. Many solder
 glasses have therefore been developed which
 have the ability to soften and flow at tem-
 peratures significantly below the deformation
 temperature of the components which they
 bond so as to cause a minimum of damage
 during the heat-sealing operation. When such
 solder glasses are those of the vitreous type,
 they are often insufficiently strong to with-
 stand the rigors of use to which the ultimate
 article is put. In addition, these solder glasses
 often have coefficients of expansion which are
 much higher than those of the components
 which they bond together. Thus, upon cool-
 ing after heat-sealing is completed, undue
 stresses are set up in the glasses further
 weakening them. In order to overcome some
 of the problems occurring with vitreous
 solder glasses, the art has developed several
 solder glasses which are initially vitreous
 but which crystallize in situ during heat-

sealing. Such in situ crystallization tends to
 strengthen the seal structure and lower the
 coefficient of expansion of the seal, thus
 bringing it more nearly into accordance with
 the components which they bond together.

In many instances and regardless of
 whether vitreous or crystallized (i.e. devitri-
 fied) solder glass seals are employed, the
 components which they bond together are
 often used to encapsulate, or are otherwise
 connected with, delicate heat-sensitive parts
 such as electronic equipment, microelectronic
 circuitry, cathodoluminescent surfaces and
 the like. To such components any increase
 in temperature experienced in their environ-
 ment is detrimental and undesirable. Thus,
 the use of heat-sealing solder glasses is by
 its very nature, a detriment to the system.
 This, of course, is also true when heat sensi-
 tive components are not present since the fac-
 tors of time and temperature are also econo-
 mic in nature. On the other hand, and in
 many instances, the advantages of using
 solder glasses over other known sealing tech-
 niques so override the detriment of heat-
 sealing that such a detriment is tolerated as
 a necessary limit upon ultimate quality. While
 this detriment is tolerated, it is of course
 always a desired end result in the develop-
 ment of any new solder glass not only to
 better its physical characteristics, but also to
 minimize the time and/or temperature of
 heat-sealing. Obviously then, the worth of
 any solder glass may be measured not only
 by its strength of bond, ability to hermetic-
 ally seal, reproducibility and the like, but
 also upon its ability to be heat-sealed at a
 minimum temperature within a minimum
 period of time.

United States Patent No. 3,250,631,
 incorporated hereinabove by reference, dis-
 closes a valuable and advantageous technique
 for reducing the coefficient of expansion of a
 devitrifiable solder glass without adversely
 affecting its sealing properties including the
 time-temperature factor in heat-sealing.

[Price 25p]

Price 25p

Thus, this patent provides the ability to match a solder glass to particular substrates without detrimentally affecting the properties of the seal or the factors involved in forming the seal. This is generally accomplished by adding to a thermally devitrifiable solder glass a sufficient amount of an inert refractory material, such as an inert refractory oxide, to lower the thermal coefficient of expansion of the solder glass to the desired, matching value without affecting the sealing temperature, flow characteristics, or other sealing properties of the solder glass.

Specifically mentioned refractory oxides are beta eucryptite and fused quartz. Preferably, the devitrifiable solder glasses are of the lead-zinc-borate type usually having a weight percent of 70—80% PbO, 7—16% ZnO; and 7—10% B₂O₃. Other oxides such as BaO, CaO, CuO, SiO₂, SnO₂, Bi₂O₃, and similar fluxes, colorants, and the like may be included in the solder glass. These glasses form excellent seals when heat-sealed at 425°C. for one hour. Generally speaking, the components sealed with these solder glasses and the solder glasses themselves are extremely versatile since they have thermal coefficients of expansion (0—300°C.) ranging from 80×10^{-7} to 120×10^{-7} in./in./°C.

The art of sealing microelectronic circuitry within ceramic components has presented special problems, especially with the advent of alumina as a ceramic component. Firstly, these ceramics generally have very low thermal coefficients of expansion (e.g. alumina ceramics vary from about $60-80 \times 10^{-7}$ in./in./°C. at 0—300°C.). Furthermore, because of the small dimensional limits of the seal and high strength and hermetic properties required, unusually stringent requirements for high strength, reproducibility and hermetic properties are placed upon any solder glass used. In addition, microelectronic circuits are very sensitive to heat, thus the time-temperature factor of heat-sealing presents more than the usual detriment to the system.

While the compositions and techniques of U.S. Patent No. 3,250,631 provide the microelectronic art with a significant improvement over known solder glasses heretofore used for ceramic (and especially alumina) component sealing, there was a definite need for improvement. While the techniques of this patent provided seals which worked when

formed at temperatures around 425—450°C. for about one hour or more, the time-temperature factor was still relatively high especially in the microelectronic circuitry art while the ability to consistently reproduce high quality seals with alumina was relatively low.

In view of the above, it is evident that there exists a need in the art for a new solder glass composition which eliminates and/or reduces the above-described problems in the sealing art generally and which is better suited to overcome the particularly acute problems in the microelectronic circuitry art more specifically.

This invention fulfils the above-described need in the art by providing certain solder glass compositions which have a materially reduced time-temperature heat-sealing factor; which forms strong, tightly hermetic, highly reproducible seals even when used to bond alumina ceramic components in microelectronic circuitry together; and which are found to be highly moisture resistant, thus increasing their life span both during storage and/or actual use. It is surprisingly and quite unexpectedly found that a significant and substantial effect is achieved both with respect to the reduction of the time-temperature factor during heat-sealing and to the ability to form a highly reproducible, strong hermetically sealed bond between ceramic components especially of the alumina type. Thus, This, not any does the subject invention unexpectedly improve the general time-temperature factor but is also, quite unexpectedly, fulfils a long felt need in the microelectronic circuitry art.

In view of the above, it can be seen that one aspect of this invention, in its broader sense, contemplates a solder glass composition which comprises an uncrystallized but crystallizable solder glass in admixture with an inert refractory material and a pre-crystallized glass, the balance, if any, consisting of other compatible ingredients preferably one or more flux and/or one or more colorant.

The crystallized but crystallizable solder glass employed may be any well known solder glass conventional in the art. Preferred solder glasses for the purposes of this invention, especially when joining alumina ceramics, are of the lead-zinc-borate type, a preferred range of ingredients being set forth in the following table:

TABLE A

	Ingredient	Brd. Range	Preferred Range	Specific Example
115	BaO	0—3	1.5—2.5	1.8
	B ₂ O ₃	5—15	8 —9	8.2
	PbO	70—85	74 —80	75.7
	SiO ₂	0—10	1 —2.5	2.0
	ZnO	5—20	10 —13	11.8

Other oxides such as CaO, CuO, SnO₂, Bi₂O₃, Na₂O, K₂O, Li₂O, CdO, and Fe₂O₃ may be included. However, it is preferred in many instances not to employ these ingredients but rather to provide compositions which consist only of those ingredients set forth in Table A.

The inert refractory materials useful in this invention may be any of such well known materials, synthetic or natural, conventional to the art. Preferably the inert refractory is a refractory oxide and most preferably is beta eucryptite or fused quartz. Of these two specifically named materials, beta eucryptite is preferred. Generally speaking, and for the best results, the refractory oxide employed decrease the expansion coefficient of the solder glass at least $15-25 \times 10^{-7}$ units.

The crystallized (pre-crystallized) glass may generally be any well known crystallized glass, devitrified in accordance with conventional techniques. Preferably, the pre-crystallized glass has the same composition as the uncrystallized glass. With respect to the lead-zinc-borate glasses described above, such are easily crystallized so as to form the pre-crystallized glasses of this invention by heating them for a period of 2 hours at 450°C.

Preferably, a thermally crystallizable glass composition blend is initially produced by a process involving the steps of providing a quantity of uncrystallized chips of crystallizable glass having a thickness of 20-25 mils, and a quantity of essentially fully crystallized glass having a particle size ranging between -20 to +80 U.S. Series Sieve screen size; reducing the particle size of the uncrystallized glass and fully crystallized glass to a particle size range as indicated; blending the fully crystallized glass particles together with the uncrystallized glass particles in a ratio of between 100-225 parts by weight of crystallized glass particles to one million parts by weight of uncrystallized glass particles to produce a uniform "master blend" of finely comminuted crystallized and uncrystallized glass particles. The "master blend" is then used for blending with the remaining amount of uncrystallized particles of thermally crystallizable glass having a composition similar to that of the "master blend" and having the same indicated particle size, the final blend being effected to ensure the presence of the indicated amount of crystallized glass in the final composition.

The crystallized glass, preferably of the same composition as the uncrystallized glass may be pre-crystallized in accordance with conventional devitrification techniques. Preferably, the glasses used are those of the lead-zinc-borate type similar to those used in U.S. Patent No. 3,250,631. These glasses are advantageously pre-crystallized by heating finely comminuted particles of the crystal-

lizable glass in a layer of 1/16 inches in thickness for 2 hours at 852°F.

Heat sealing using the above-described blended solder glass can be effected at 425°C. for 20-50 minutes. Such a heat-sealing represents a significant decrease in time without a significant increase in temperature.

The specific weight percents actually employed of each component of the solder glass compositions of this invention will vary over a wide range depending upon the ultimate environmental factors of use. Generally speaking, a sufficient amount of refractory oxide and pre-crystallized glass should be added such that together they provide the necessary coefficient of expansion match-up, flow properties, and crystallization speed to decrease the normal time-temperature factor of the heat-sealing process while at the same time provide a strong, tightly hermetic, moisture-resistant seal.

Exemplary of a range of ingredients for most contemplated purposes includes by weight percent: 5-15% refractory material, 0.0001-0.03% pre-crystallized glass, and 85-95% uncrystallized glass. In a preferred embodiment, the ranges are 7-11% refractory material, .02% pre-crystallized glass, and 89-93% uncrystallized glass.

The glass compositions of this invention are usually in particulate form and are formulated by blending particles of the various constituents together. Generally speaking for best results, all particles of all constituents should be less than 100 U.S. Series Sieve screen in size. Preferably, 50 percent by weight of all particles should be less than 325 U.S. Series Sieve screen in size but less than 5% by weight smaller than 5 microns. For best results especially when sealing alumina ceramics, the particles of at least the base uncrystallized solder glass and preferably of all constituents should be reduced such that at least 70% by weight are smaller than 400 U.S. Series Sieve screen but less than 3.0% by weight are smaller than 3 microns. Achievement of the necessary particle sizes is obtainable in accordance with well-known fritting and grinding techniques.

The compositions of this invention may be blended in accordance with any conventional technique. However, for best results uniform dispersion of at least the pre-crystallized glass and preferably the refractory material should be employed. This is most conveniently accomplished by making a "master blend" of the pre-crystallized and uncrystallized glass chips such that the pre-crystallized glass is present in an amount of 100-225 parts by weight of crystallized glass particles to one million parts by weight of uncrystallized glass chips, the particle size being in the order of -20 to +80 U.S. Series Sieve screen size. Thereafter, the comminution and blending may be carried out simultaneously in a suit-

able mill such as a ball mill. In a like manner, a blend of uncrystallized glass particles and refractory material particles is formulated. The two blends are then admixed in the requisite quantities and mixed using any conventional technique e.g. a paint shaker. As an alternative, the "master blend" may be admixed in one step with the remaining ingredients with separate formulation of the refractory blend.

The glass compositions so formed as above-described are capable of forming seals which in one aspect solve a long felt need in the microelectronic circuitry art. Generally speaking, the time-temperature factor for a given system is significantly reduced usually by a factor at least as high as 1.5. Representative of the reduced time-temperature factor unexpectedly achieved as the fact that for most solder glasses and refractory systems employed sealing is effected at 400–500°C. with crystallization being substantially completed within about 1–60 minutes. In a preferred form of this invention and when using the preferred glass compositions hereinabove described heat sealing to a strong, hermetically tight, reproducible seal is effected in e.g. 8 min. at 450°C. or 30 min. at 425°C.

By the term "crystallization substantially completed" is meant crystallization to the extent necessary to achieve the requisite strength and thermal coefficient of expansion. The term "hermetically tight" is defined by Military Standard Test No. 883 which in one instance (without thermal shock) defines hermetically tight as helium leakage less than about 1×10^{-8} cc/sec. He.

The solder glass compositions of this invention may be applied to their substrates by any conventional technique. Examples of such techniques include spraying, screen-printing, and pyrolyzable tapes. In forming the compositions into sprayable slurries, they are usually dispersed in a liquid organic medium such as alcohol to a sprayable viscosity. Another example of a slurry medium is 1-1/2% nitro-cellulose in amyl acetate. Any of the conventional paste organic vehicles may be employed for forming a paste while conventional tapes may also be used.

Once the material is applied, it is dried and/or heated in accordance with conventional techniques to burn off the vehicle and then fired to devitrify the seal. A particularly preferred heat cycle for devitrifying a seal according to this invention comprises a heat up time of 75–100°C./min., a hold as indicated at peak temperature, and a cooldown rate of 50–60°C./min. Such a heat cycle usually ensures a high quality seal and a reasonable minimization of weakening stresses being effected during cooling.

The following examples are presented by way of illustration rather than limitation.

EXAMPLE 1

A base glass is formulated from the following composition expressed in percent by weight:

	Percent
SiO ₂	2.00
ZnO	11.80
PbO	75.69
B ₂ O ₃	8.20
BaO	1.80

by heating the requisite amounts of raw batch ingredients in a platinum crucible at about 1800°F. in an air atmosphere for one and one-half hours. The glass is then fritted and ground to a particle size such that greater than 70% by weight of the particles are less than 400 U.S. Series Sieve screen in size. After grinding, the glass powder has the following profile:

% Ogives ¹	Micron Size
90	60
80	43
75	38
60	28
50	22
40	17
25	11
20	9.4
10	6.0
5	4.3
2	3.0

1. Percent ogives is the accumulation (the sum) of all frequencies up to and including the specific frequency in the frequency distribution. Thus, for example, 90% ogives indicate that 90% of the particles have a micron size of 60 or less.

Screen Mesh	%
100	< trace
140	0.8
200	4.8
270	7.6
325	5.0
400	10.5
—400	71.3

499 grams of this powder is then blended with 1 gram of the above-described glass composition previously crystallized to form a "master blend". The pre-crystallized glass composition is previously devitrified by taking 10 grams of the vitreous glass powder and pressing it at 1000 psi into a 3/4" diameter button which is thereafter heated at 450°C. for 2 hours to ensure that devitrification is completed. The button is then fritted and ground to a particle size similar to that of the vitreous glass powder to which it is added. The "master blend" (500 grams) so formed is thoroughly mixed by ball milling for 15 minutes.

Separate from the "master blend" is formulated an admixture of 400 grams of the vitreous glass powder and 50 grams of beta-eucryptite previously ground to a particle size similar to the glass powder to which it is added. The "master blend" and beta-eucryptite containing powder are then blended together for 15 minutes using a paint shaker so that the final blend contains 0.02% by weight crystallized glass powder and 10% beta-eucryptite.

The powder is then formed into a printing paste by admixing it with an organic vehicle consisting of an organic binder and a liquid solvent therefor. The paste consists of a weight ratio of 6.5:1 powder to vehicle. The resulting paste is then screen-printed onto a base and cap of alumina (thermal coefficient expansion = 64×10^{-7} in./in./°C 0—700°C.) using standard techniques and a screen of 80 mesh.

The printed coatings are then dried at 330°C. for 15 minutes to remove the organic solvent and fired at 440°C. for 6 minutes to drive off the organic binder. No substantial amount of crystallization takes place at this time. This second step is optional where an organic binder is present. In the case of an alcohol slurry, a single drying step of 125°C. for 15 minutes is all that is necessary. The base alumina substrate is then provided with conventional electronic lead frames while the cap alumina substrate is inverted upwardly and the base and lead frames brought into contact therewith. The package is then heated at a rate of 100°C./min. to a peak of 450°C. and held for 8 minutes at this temperature to crystallize the seal. The package is then completed by cooling at a rate of 60°C./min. to room temperature. The structure is then subjected to testing in accordance with the following Example.

EXAMPLE II

The structure formed in Example I was subjected to Military Standard Test No. 883

by using both test condition A to test for fine cracks and test condition C to test for large cracks. In conducting test condition A, the structure is placed in a pressure chamber and subjected to a He. pressure of 75 psi for 1 hour after which the structure is removed and "rinsed" with N₂ gas. The structure is then tested in a standard Helium Leak Detector for traces of helium. In conducting test condition C, the structure after being tested under condition A is submerged in a beaker of silicone oil at 125°C. and any bubbles emerging from the structure are observed.

When so tested, the structure under test condition A passed the test in that it indicated a helium leakage of less than 1×10^{-8} cc/sec. He. The structure also passed test condition C in that no bubbles were observed.

In addition to the above testing, the structure was subjected to a thermal shock test consisting of initially immersing the structure in boiling water for 1 minute and then quenching in ice water within 5 seconds. The cycle is repeated four additional times. Test conditions A and C were then repeated and the structure again passed these tests, thus indicating the unusually strong nature of the sealing qualities of this invention despite the fact that the time-temperature factor is materially reduced over those known factors in the prior art.

EXAMPLE III

In order to illustrate the invention, a standard differential thermal analysis (D.T.A.) and differential scanning calorimetry test (D.S.C.) were run on several compositions including those representative of U.S. Patent No. 3,250,631, the prior art and this invention. These tests are adequately described in the publication by DuPont Instrument Products Division entitled DU PONT 900 DIFFERENTIAL THERMAL ANALYZER. The equipment used was that of this manual. The compositions tested and results are set forth in TABLE B.

TABLE B

Constituents (% wt.)	1	2	3	4
BaO	1.8	1.8	1.8	1.8
B ₂ O ₃	8.2	8.2	8.2	8.2
PbO	75.69	75.69	75.69	75.69
SiO ₂	2.00	2.00	2.00	2.00
ZnO	11.80	11.80	11.80	11.80
% Ref. Oxide	0	0	10	10
% Cryst. Glass	0	0.02	0	0.02
DTA (major peaks min.)	42.5	19.0	12.0	10.5
Completion time (min.)	54.5	25.0	41.5	23.5
DSC				
A. Major peak (min.)	32.5	19.5	10.25	11.5

	Constituents (% wt.)	1	2	3	4
	B. Area under isothermal curve °C.				
	min./100 gr.	9.7	10.1	5.5	8.1
5	Stress of seal p.s.i.	3400T	3400T	400—750C	1300C
T=tension		C=compression			

10 The compositions included the base glass as indicated admixed in accordance with the techniques described above relative to blending; particle size and the like, with the indicated amount of additive. Thus the amount of additive given is that of the overall blended composition. In each instance, particle sizes between compositions were the same and the crystallized glass had a composition the same as that of the base glass employed. The pre-crystallized glass was devitrified by heating at 450°C. for 2 hours.

20 The relative stress data reported was measured by the conventional glass rod-stress technique wherein a small mound of the indicated glass is fired upon the end of a standard glass rod having a coefficient of expansion of 83×10^{-7} in./in./°C. and cooled. 25 The heating range is 10°C./min. to 450°C. for 30 minutes then cooled at 5°C./min. to room temperature. The stress is measured by standard optical techniques. Compression 30 indicates a lower coefficient of thermal expansion than the base glass while tension indicates a higher coefficient of thermal expansion. Since about 200 psi equals 1 expansion point, in order to form a strong seal with 35 conventional alumina substrates (on the order of $60-80 \times 10^{-7}$ in./in./°C.), the test should indicate a compression of greater than about 800 psi.

40 The results reported in the above table clearly show the nature of this invention. Firstly, it can be seen that the beta-eucryptite example (No. 3) is in compression of about 400—750 psi. On the other hand, the pre-crystallized glass example (No. 2) is in tension of about 3400 psi. One would therefore expect that if runs No. 2 and No. 3 were combined a stress either equal that of Run No. 3 or intermediate these two values and probably tending toward tension would result. 50 To the contrary, and quite unexpectedly, not only does the combination, as per this invention, result in a compression much greater than even the beta-eucryptite alone, but is of such compression as to make it ideally suitable for use with alumina substrates conventional in microelectronic circuitry. 55

As a further indication of the unexpected effects of this invention is the DTA and DSC data taken as a whole. This data indicates that beta-eucryptite additive forms either a lower amount of crystals, different crystals or a combination of both than does

either the base glass alone or with pre-crystallized glass added thereto (the two being of the same magnitude). Thus one would surmise that if beta-eucryptite were used with the pre-crystallized additive the composite would assume crystalline characteristics close to the beta-eucryptite since the pre-crystallized glass did not substantially affect the crystalline nature of the base glass used alone. Contrary to this expectation, and quite unexpectedly to the betterment of the system, the combination results in crystallization characteristics quite close to those of the base glass and base glass plus pre-crystallized glass either by way of quantity, type of crystallization or both. Such "familiar" as opposed to "foreign" crystallization greatly improves the quality of reproducibility which is one of the main detriments to the use of beta-eucryptite alone as an additive. Further indication of "foreign" crystallization was represented by a lack of a secondary peak for run No. 3 in the DSC test. 65 70 75 80 85

In addition to the above, not only does the combination unexpectedly do away with the detrimental effects of beta-eucryptite as evidenced by the area under the isothermal curve, but it also unexpectedly lowers the time-temperature factor as evidenced by actual test results hereinbefore reported as well as the peak and completion time data from the DTA and DSC tests. 90

Note in this respect, that the combination is much faster than the swift pre-crystallized run (No. 2) despite the fact that beta-eucryptite (which results in a slower completion time than the pre-crystallized run, when used alone) is added thereto. 100

Once given the above examples, many other features, modifications and improvements will become apparent to those skilled in the art. Such other features, modifications, and improvements are considered to be a part of this invention, the scope of which is to be determined by the following claims: 105

WHAT WE CLAIM IS:—

1. A solder glass composition comprising an uncrystallized but crystallizable solder glass in admixture with an inert refractory material and a pre-crystallized glass, the balance if any, consisting of other compatible ingredients. 110

2. A solder glass composition as claimed in Claim 1 wherein the amounts by weight 115



	Constituents (% wt.)	1	2	3	4
	B. Area under isothermal curve °C.				
	min./100 gr.	9.7	10.1	5.5	8.1
5	Stress of seal p.s.i.	3400T	3400T	400—750C	1300C
	T=tension	C=compression			

10 The compositions included the base glass as indicated admixed in accordance with the techniques described above relative to blending, particle size and the like, with the indicated amount of additive. Thus the amount of additive given is that of the overall blended composition. In each instance, particle sizes between compositions were the same and the crystallized glass had a composition the same as that of the base glass employed. The pre-crystallized glass was devitrified by heating at 450°C. for 2 hours.

15 The relative stress data reported was measured by the conventional glass rod-stress technique wherein a small mound of the indicated glass is fired upon the end of a standard glass rod having a coefficient of expansion of 83×10^{-7} in./in./°C. and cooled. The heating range is 10°C./min. to 450°C. for 30 minutes then cooled at 5°C./min. to room temperature. The stress is measured by standard optical techniques. Compression indicates a lower coefficient of thermal expansion than the base glass while tension indicates a higher coefficient of thermal expansion. Since about 200 psi equals 1 expansion point, in order to form a strong seal with conventional alumina substrates (on the order of $60-80 \times 10^{-7}$ in./in./°C.), the test should indicate a compression of greater than about 800 psi.

20 The results reported in the above table clearly show the nature of this invention. Firstly, it can be seen that the beta-eucryptite example (No. 3) is in compression of about 400—750 psi. On the other hand, the pre-crystallized glass example (No. 2) is in tension of about 3400 psi. One would therefore expect that if runs No. 2 and No. 3 were combined a stress either equal that of Run No. 3 or intermediate these two values and probably tending toward tension would result. To the contrary, and quite unexpectedly, not only does the combination, as per this invention, result in a compression much greater than even the beta-eucryptite alone, but is of such compression as to make it ideally suitable for use with alumina substrates conventional in microelectronic circuitry.

25 As a further indication of the unexpected effects of this invention is the DTA and DSC data taken as a whole. This data indicates that beta-eucryptite additive forms either a lower amount of crystals, different crystals or a combination of both than does

either the base glass alone or with pre-crystallized glass added thereto (the two being of the same magnitude). Thus one would surmise that if beta-eucryptite were used with the pre-crystallized additive the composite would assume crystalline characteristics close to the beta-eucryptite since the pre-crystallized glass did not substantially affect the crystalline nature of the base glass used alone. Contrary to this expectation, and quite unexpectedly to the betterment of the system, the combination results in crystallization characteristics quite close to those of the base glass and base glass plus pre-crystallized glass either by way of quantity, type of crystallization or both. Such "familiar" as opposed to "foreign" crystallization greatly improves the quality of reproducibility which is one of the main detriments to the use of beta-eucryptite alone as an additive. Further indication of "foreign" crystallization was represented by a lack of a secondary peak for run No. 3 in the DSC test.

30 In addition to the above, not only does the combination unexpectedly do away with the detrimental effects of beta-eucryptite as evidenced by the area under the isothermal curve, but it also unexpectedly lowers the time-temperature factor as evidenced by actual test results hereinbefore reported as well as the peak and completion time data from the DTA and DSC tests.

35 Note in this respect, that the combination is much faster than the swift pre-crystallized run (No. 2) despite the fact that beta-eucryptite (which results in a slower completion time than the pre-crystallized run, when used alone) is added thereto.

40 Once given the above examples, many other features, modifications and improvements will become apparent to those skilled in the art. Such other features, modifications, and improvements are considered to be a part of this invention, the scope of which is to be determined by the following claims:

WHAT WE CLAIM IS:—

1. A solder glass composition comprising an uncrystallized but crystallizable solder glass in admixture with an inert refractory material and a pre-crystallized glass, the balance if any, consisting of other compatible ingredients.

2. A solder glass composition as claimed in Claim 1 wherein the amounts by weight

are: 5—15% refractory material, 0.0001—0.03% pre-crystallized glass, and 85—95% crystallizable glass.

3. A solder glass composition as claimed in Claim 1 or 2 wherein the amounts by weight are: 7—11% refractory material, 0.02% pre-crystallized glass, and 89—93% crystallizable glass.

4. A solder glass composition as claimed in any one of Claims 1 to 3 wherein the inert refractory material is a refractory oxide.

5. A solder glass composition as claimed in Claim 4 wherein said refractory material is fused quartz.

6. A solder glass composition as claimed in Claim 4 wherein said refractory material is beta-eucryptite.

7. A solder glass composition as claimed in any one of Claims 1 to 6 wherein the particle size of all constituents is less than 100 U.S. Series Sieve screen.

8. A solder glass composition as claimed in any one of Claims 1 to 7, wherein the particle size of 50 percent by weight of all constituents is less than 325 U.S. Series Sieve screen in size but less than 5% by weight are smaller than 5 microns.

9. A solder glass composition as claimed in any one of the preceding claims wherein the particles size of at least 70% by weight of all constituents is less than 400 U.S. Series Sieve screen but less than 3.0% by weight are smaller than 3 microns.

10. A solder glass composition as claimed in any one of the preceding claims wherein said pre-crystallized glass has the same composition as said crystallizable solder glass.

11. A solder glass composition as claimed in any one of the preceding claims wherein said crystallizable solder glass is a lead-zinc-borate glass.

12. A solder glass composition as claimed in any one of the preceding claims wherein said crystallizable solder glass consists essentially of by weight: 0—3% BaO, 5—15% B₂O₃, 70—85% PbO, 0—10% SiO₂ and 5—20% ZnO.

13. A solder glass composition as claimed in Claim 12 wherein said crystallizable solder glass composition consists essentially of by weight: 1.5—2.5% BaO, 8—9% B₂O₃, 74—80% PbO, 1—2.5% SiO₂ and 10—13% ZnO.

14. A solder glass composition as claimed in Claim 13 wherein said crystallizable solder glass consists essentially of by weight: 1.8% BaO, 8.2% B₂O₃, 75.7% PbO, 2.0% SiO₂ and 11.8% ZnO.

15. A solder glass composition as claimed

in any one of the preceding claims wherein said compatible ingredients comprise one or more colorant.

16. A solder glass composition as claimed in any one of the preceding claims wherein said compatible ingredients comprise one or more flux.

17. A solder glass composition as claimed in any one of Claims 1 to 11 wherein said crystallizable solder glass comprises by weight 70 to 80% PbO, 7 to 16% ZnO; and 7 to 10% B₂O₃, the balance, if any consists of any one of BaO, CaO, CuO, SiO₂, SnO₂, Bi₂O₃, and similar fluxes and colorants, or mixtures thereof.

18. A solder glass composition as claimed in Claim 1 and substantially as hereinbefore described with reference to and as illustrated in Example I or III (4).

19. A method of forming a tight, strong substantially hermetic seal between two substrates which comprises forming a layer of a composition of any one of Claims 1 to 18, inclusive between said substrate and heating said composition for 1—60 minutes at a temperature of 400—500°C.

20. A method as claimed in Claim 19 wherein the solder glass composition is formulated by forming an intimate master blend of crystallized particles and a portion of said crystallizable glass particles comprising 100—225 parts by weight of crystallized particles to one million parts by weight of said crystallizable particles and thereafter forming an intimate admixture of said master blend with the remaining portion of crystallizable particles and said refractory material.

21. A method as claimed in Claims 19 or 20 wherein at least one of said substrates is an alumina substrate in a microelectronic package.

22. A method as claimed in any one of Claims 19 to 21 wherein said heating is for 8 minutes at 450°C.

23. A method as claimed in any one of Claims 19 to 21 wherein said heating is for 30 minutes at 425°C.

24. A method of forming a tight, strong substantially hermetic seal between two substrates as claimed in Claim 19 and substantially as hereinbefore described with reference to and as illustrated in Example I.

25. A method of making a glass composition as claimed in any one of Claims 1 to 18 which comprises admixing an uncrystallized but crystallizable solder glass, an inert refractory material and a pre-crystallized glass.



26. A method of making a glass composition substantially as hereinbefore described with reference to and as illustrated in Example I.

W. P. THOMPSON & CO.,
12, Church Street,
Liverpool, L1 3AB.
Chartered Patent Agents.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1973.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

