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(54) METHOD OF BONDING GLASS ARTICLES TOGETHER

(71) We PHILIPS ELECTRONIC AND ASSOCIATED INDUSTRIES LIMITED of Abacus House, 33 Gutter Lane, London, E.C.2. 8AH a British Company, 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:

The invention relates to a method of bonding glass articles together and to an assembly of glass articles bonded together by such a method.

German Patent Application 2,331,414 which has been laid open to public inspection discloses such an assembly which consists of glass articles and an intermediate thermoplastic material which wets the surfaces of these glass articles and constitutes a connection between them.

This thermoplastic material may consist of a polymer, such as a polycarbonate, poly(methyl methacrylate) or poly(butylene terephthalate).

In practice, however, it appears that the bond obtained cannot satisfy a stringent requirement with respect to chemical stability and thermal load. In general the adhesion is not very good; it is easy to separate plates which have been bonded by means of polyethylene, using a sharp object to effect separation. Even in cold water such a bond is rather easily disrupted.

The invention provides a method of bonding glass articles together by means of a polyethylene film, wherein the glass articles consist of oxidic glass, of which a surface layer not more than 300 Å thick has a composition which is deficient in lattice-forming and/or lattice-modifying ions relative to oxygen ions, and the articles are bonded together at a temperature between 125 and 250°C under a pressure of at least 5 g/mm^2 by means of a polyethylene film whose surface has been modified by processing with an oxidizing agent.

It was found that assemblies of glass articles bonded together by the method according to the invention met very stringent requirements. Depending on the type of glass. the bond withstands a 100 to 200 hours life test consisting of cycles of 30 minutes at -20°C followed by 120 minutes in boiling water.

During the investigations which led to the invention, it appeared that glasses having high contents (more than 80 mol.%) of lattice-forming oxides (siO_2, B_2O_3, Al_2O_3) naturally have already a surface composition which is deficient in lattice-modifying ions with respect to the oxygen ions as compared to the mass of the relevant glass parts. It appeared that this type of glass, for example quartz glass and other hard glasses, for example of the borosilicate type can be bonded together without further measures by means of superficially modified polyethylene. In the surface layer the atomic share of metal is approximately half of that in the glass mass. The surface layer where this metal deficiency is found is only a few tens of Å thick and the deficiency varies from the outside to the inside, of this surface layer.

In glasses, such as lime glass, which contain a large proportion of alkali metal oxides and alkaline earth metal oxides, such a metal deficiency does not occur. Consequently it is not possible to bond together articles consisting of these glasses in an untreated state by means of polyethylene film. However, by means of prior art measures a metal deficiency can be created in a surface layer of this type of glass. By means of such measures, such as by processing with a strong lye (pH > 10) and thereafter replacing metal ions by H^+ ions by bringing them into contact with a solution of an acid, or by keeping the glass articles for some time in contact with moist sulphur dioxide-containing air (German patent 1,156,946), the articles can be bonded by means of superficially modified polyethylene by the method according to the invention.

According to a further embodiment of the invention the surface of the pre-treated polyethylene and/or the glass surface which is deficient in metal is treated with an organosilane, by hydrolysing this compound of, for example, the structure $RSiX_3$, where R is $-(CH_2)_3NH_2$ or $-(CH_2)_2-\underbrace{CH-CH_2}_{O}$ and X is a halogen or OR′, where R′ is alkyl, preferably methyl, ethyl or propyl, in water, on the glass surface or in the gas phase. This results in compounds of the type $RSi\,X_{(3-n)}(OH)_n$, where n = 1, 2 or 3, which effect a still more stable bond between the glass and the polyethylene. This results in a considerable prolongation of the life of the bond especially in a moist environment.

By means of modern methods of physical analysis, for example secondary ion-mass spectroscopy (SIMS) it is possible to determine the composition of the glass in a surface layer of only a few tens of Å. Listed below, by way of illustration, are the analysis results for two types of glasses, namely a borosilicate glass of the composition expressed in percent by weight:

(2)	SiO_2	78.9	K_2O	1.2
	B_2O_3	14.4	MgO	0.3
	Na_2O	3.5	Al_2O_3	1.7

and a lime glass of the composition expressed in percent by weight

(4)	SiO_2	68.0	BaO	2.0
	Na_2O	16.8	MgO	3.9
	K_2O	1.0	Al_2O_3	2.6
	CaO	5.7		

The following analyses were made of these two glasses:

i) of a cross-section in the mass of the glass;
ii) of a surface portion at a depth of approximately 50 Å;
iii) of the surface after it had been processed for 1 hour in 1 *N* KOH at 50°C;
iv) of the surface portion after it had been processed for 1 hour in a mixture of 60°C of 1:1:2, in volume parts, HNO_3 (d = 1.43), H_2SO_4 (d = 1.84) and water.

Glass compositions	(2)		(4)		
	i	ii	i	ii, iii	iv
Si	24.6	14.2	23.6	16.8	8.8
Na	3.0	2.3	11.3	18.5	11.6
K	0.5	1.8	0.4	1.1	1.1
Ca			2.1	1.3	0.9
B	7.8	3.8			
Al	0.6	0.3			
Mg	0.015	0.018			
O (computed)	balance	balance	balance	balance	balance
oxygen/metal	1.7	3.4	1.4	1.4	2.9
free OH of each metal on the surface.		1.7		0	1.5

Polyethylene is available in many grades, in which the degree and manner of polymerisation, that is to say predominantly in the form of elongated chains, highly branched chains or all kinds of intermediate forms, may differ. In the currently used methods a distinction is made between the "low-pressure method" and the "high-pressure method", these methods generally result in products of a high density or products of a low density respectively. Tests within the scope of the invention proved that in this respect those varieties are equivalent.

The method according to the invention may be used for the production of cuvettes for displays or for spectrophotometry or for the fabrication of slide holders for microscopes.

Some embodiments of the invention will now be described with reference to the following Examples.

EXAMPLE 1

Two sheets of lime glass having the composition (4) defined above were first processed for one hour in an aqueous 1 *N* KOH solution at 50°C and thereafter for another hour at 60°C in a mixture in the ratio by volume 1:1:2 HNO_3 (*d* = 1.43), H_2SO_4 (*d* = 1.84) and water. The symbol *d* signifies the density expressed in g/ml.

Polyethylene film, 20 μm thick was degreased in acetone for two minutes at 20°C, rinsed in demineralised water and dried thereafter. Subsequently the film was kept into contact for one minute with a solution having a temperature of 60°C, which contained 85% by weight of H_2SO_4, 2.5% by weight of potassium bichromate and 12.5% by weight of water and was then rinsed. Subsequently the film was brought into contact with a solution of 0.2% by weight of γ-aminopropyl-triethoxy-silane in water so that it was hydrolysed, whereafter it was dried at 50°C.

Finally the two glass sheets with the intermediate film were kept for eight minutes under a pressure of 1.2 kg/m^2 while heated to 160°C. A highly transparent bond was obtained. The shear strength, determined by a tangential displacement at 25°C, was 160 kg/cm^2 of adhesive surface area. After a few weeks the bond stabilised at a value of 100 kg/cm^2 surface area. In a life test consisting of one year's storage at room conditions or a life test at a relative humidity of 100% and a temperature of 55 ± 3°C for 16 hours and 8 hours at 20°C per 24-hour period, no measurable change in the bond could be observed.

A comparable result was obtained with glass sheets having the composition (expressed in percent by weight) (1):

SiO_2	70.3	BaO	2.8
Na_2O	9.0	Al_2O_3	0.2
K_2O	7.4	Sb_2O_3	0.6
CaO	9.7		

EXAMPLE 2

Two glass sheets having the composition (2) (defined above) where first degreased by keeping them for 5 minutes in contact with a 1% by volume aqueous solution of Teepol (Trade Mark), i.e. the Na-salt of a secondary alkyl sulphate, whereafter they were kept in 1 *N* KOH at 50°C for 1 hour, rinsed and dried. As in the previous Example, polyethylene film, 20 μm thick was degreased in acetone, and was then kept for 5 minutes in a solution having a temperature of 60°C, which contained 52.5% by weight of H_2SO_4 (d = 1.84), 5.5% by weight of $Na_2Cr_2O_7$ and 42% by weight of H_2O, whereafter the film was rinsed and dried at 50°C for half an hour.

The glass sheets with intermediate film were compressed at a pressure of 1.2 kg/cm^2 and the assembly was heated to 160°C for 6 minutes. A highly transparent bond was obtained. At 25°C a force of 100 kg/cm^2 of adhesive surface area was required to separate the sheets from one another by displacing the sheets in a tangential direction.

The sheets were subjected to a life test, consisting of 30 minutes at -20°C in air and 120 minutes in boiling water. The bond was still intact after 80 of these cycles.

The shear strength at a tangential load was also not affected by a life test consisting of storage for 1 year at room conditions.

If the glass according to this example is processed in exactly the same manner as in the previous Example, that is to say kept into contact with an acid mixture after the KOH-treatment, then the tangential tensile strength obtained was 160 kg/cm^2.

EXAMPLE 3

In this example a plurality of glass sheets of the following compositions (expressed in percent by weight) were used as starting material. All the sheets (2 of each composition) were degreased by keeping them in contact with 1 *N* KOH at 60°C for 1 hour. After degreasing only the lime glass sheets (4) were exposed for some time to moist sulphur dioxide-containing air and rinsed thereafter.

Polyethylene film, 20 μm thick was degreased by rinsing it for 2 minutes in acetone at 20°C, rinsed thereafter in demineralised water, processed for 5 minutes at 60°C in a solution which contained 52.5% by weight of H_2SO_4 (d = 1.84), 5.5% by weight of $Na_2Cr_2O_7$ and 42% by weight of water, rinsed in water and dried at 50°C for half an hour.

Each time two sheets of glass of the same kind with intermediate film were compressed with a pressure of 1.2 kg/cm^2 and the assembly was heated to 160°C for 8 minutes. In all cases a highly transparent bond was obtained.

For all combinations the tangential shear strength was approximately 160 kg/cm^2 of adhesive surface area, measured at 25°C. After a life test for 50 hours in water at 100°C, this value decreases to about 85 kg/cm^2.

If the film is silanized in the manner described in Example 1, the shear strength decreases to 100 kg/cm^2 after said life test.

The various combinations were also subjected to the life test consisting of 30 minutes in air at -20°C followed by 120 minutes in boiling water. The quartz glass bond loosened after 80 cycles, the G 28 (3) bonds after 60 cycles, the lead glass (5) bond after 50 cycles, the BK7 (6) bond after 70 cycles, and with the lime glass (4) which was processed in SO_2 in the manner specified above, the bond loosened after 70 cycles.

WHAT WE CLAIM IS:—

1. A method of bonding glass articles together by means of a polyethylene film, wherein the glass articles consist of oxidic glass, of which at least a surface layer not more than 300 Å thick has a composition which is deficient in lattice-forming and/or lattice-modifying ions relative to oxygen ions, and the articles are bonded together at a temperature of between 125 and 250°C under a pressure of at least 5 g/mm^2 by means of polyethylene film which is between 5 and 100 μm thick and whose surface has been modified by processing the polyethylene film with an oxidizing agent.

2. A method as claimed in claim 1, wherein the surface modified polyethylene film or the glass is processed with an organosilane.

3. 3, A method of bonding glass articles together by means of a polyethylene film, substantially as herein described with reference to any of Examples 1 to 3.

4. An assembly consisting of glass articles bonded together by a method as claimed in any preceding claim.

Sample:	SiO_2	B_2O_3	Na_2O	K_2O	CaO	BaO	MgO	PbO	Al_2O_3	As_2O_3	Sb_2O_3
G 28 (3)	64.7	23.1	5.5	2.8					3.9		
lime-glass (4)	68.0		16.8	1.0	5.7	2.0	3.9		2.6		
lead-glass (5)	57.0		8.0	4.5	0.1		0.2	28.5	1.4		0.3
BK7 (6)	69.0	10.0	9.0	8.3		3.4				0.3	
quartz-glass (7)	99.6								0.4		

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