

SPECIFICATION

Method of handling or shaping glass

- 5 The invention relates to methods of handling or shaping glass at low viscosities, using tools such as dies, moulds, blow moulds and shears for cutting off glass blobs, these tools comprising, at least in a surface layer a boron-containing material.
- 10 The glass must not stick to the tools used during the manufacture of glass articles, and films of boron nitride have been used hitherto to prevent this (U.S. patent specification 2,201,049). These films have the drawback that they must be regularly renewed and
- 15 that they cause extensive contamination of the glass surface. Moreover, boron nitride has a low mechanical strength. The above-mentioned low viscosities are understood to mean viscosities in the range from 10^8 to 10^9 Pa.s (10^2 to 10^{10} poises), at these values the
- 20 glass ranges from being in a fluid state to being just softened.
- United Kingdom patent specification 1,045,803 describes and claims a process for the hot working of glass, wherein there is interposed, between the
- 25 hot glass and a mechanical part with which the glass would otherwise come into contact, a readily fusible vitreous substance comprising boric anhydride.
- An object of the invention is to provide a method of handling or shaping glass, in which method the
- 30 tools used do not contaminate the glass surface to an unacceptable extent.
- The invention provides a method of handling or shaping glass at viscosities in the range from 10^8 to 10^9 Pa.s (10^2 to 10^{10} poises) with the aid of a tool
- 35 comprising at least in a surface layer at all areas in contact with the glass a boron-containing material which is a boride containing at least 5 atom % boron, boron carbide, or a boron-containing alloy containing at least 5 atom % boron.
- 40 When this surface layer of a tool used in a method according to the invention is contacted with an oxidizing medium at a temperature above 450°C , a film of liquid oxide B_2O_3 is formed. It is, alternatively possible to form the B_2O_3 film by applying an electric
- 45 field between the tool and the glass melt. This film has a low intrinsic strength relative to glass with which it is in contact. The bond with the glass can be easily broken in this film. However, it should be borne in mind that the B_2O_3 , depending on the composition of the glass and the temperature, may dissolve in the glass more or less readily, or *vice versa*.
- 50 Therefore, the tools must not be in contact with the glass for such a length of time that the low-viscosity intermediate layer has disappeared. Consequently,
- 55 the method according to the invention is restricted to uses where the contact between the tool and the glass is relatively short, such as where the tool is a die or a mould.
- In one aspect of the invention, the surface of the
- 60 tool is coated with a thin layer of inert material where through the boron from the boron-containing material can preferentially diffuse. On oxidation, the desired oxide, B_2O_3 , forms predominantly at the surface. The inert material may *inter alia* be palladium.
- 65 In another aspect of the invention, a tool is used

which comprises at least in a surface layer, a wear-resistant, porous material, and the pores of this surface layer contain the boron-containing material or the B_2O_3 formed therefrom.

- 70 Porous, sintered tungsten or molybdenum can be loaded in this manner with boron, in the form of one of the above-mentioned boron-containing materials. This aspect of the invention has the advantage that, when all the boron has been used up, the material of
- 75 the tool can again be provided with boron in a simple manner. In the above-defined aspects of the invention, the tool has, indeed, a very long life, but this life is nevertheless finite owing to boron consumption by oxidation.
- 80 Some embodiments of the invention will now be described with reference to the following Examples, and to the drawing, in which the single Figure is a graph illustrating the variation of the force necessary to break a bond between a glass and different materials with temperature.
- 85

EXAMPLE 1

Bodies consisting of different boron-containing materials were contacted at different temperatures for 20 seconds with a glass having a composition

90 (expressed in percent by weight) as specified below, this glass being used for making face-plates of cathode-ray tubes used for the display of television pictures.

95	SiO_2	64.0	MgO	1.2
	Na_2O	9.6	Al_2O_3	3.5
	K_2O	6.5	Sb_2O_3	0.6
	CaO	1.8	CeO_2	0.2
	BaO	12.4	SrO	0.2

- 100 This glass has the following viscosity values: η being the viscosity of the glass expressed in Pa.s.
 $\log \eta = 12.5$ at 465°C (the annealing temperature)
 $\log \eta = 6.65$ at 690°C (the softening temperature)
 $\log \eta = 3$ at 1000°C (the working temperature).
- 105 The following materials were tested for use with this glass: B_4C , a Ni-B alloy (81.5 atom % Ni and 18.5 atom % B), a Ni-Cr-B-alloy (Ni 69.3, Cr 14.5 and B 16.2 atom %), Pd-B, containing 95 atom % Pd and 5 atom
- 110 % B, titanium boride and titanium boride coated with an approximately $3\mu\text{m}$ thick Pd layer.
- The force necessary to break the bond was measured. The accompanying graph shows the force expressed in MPa (megaPascals) which was calculated from the measured force and the area of the
- 115 contacting surface. Measurements of the bond of glass to some properly adhering materials (SiC , Si_3N_4 and Fe-Cr-Ni) are also shown for comparative purposes. An important criterion therein is whether
- 120 the adhesion is less than the strength of the glass. As an indication thereof, the graph also shows in a rough approximation, the strength of the glass as a function of the temperature (G1). The time the material was in contact with the glass was 20 seconds. The
- 125 graph shows that the group of boron-containing materials has a decreasing bond strength with increasing contact temperature, whereas the materials which form a fixed oxide skin have a bond strength which increases with increasing temperature.
- 130 In the latter group the breaking strength at high

temperatures is determined by the strength of the glass. The loss of thickness of a layer of B_4C by oxidation in air at $1000^\circ C$ is approximately $1\mu m/hour$.

EXAMPLE 2

- 5 Tools of wear-resistant porous material (such as tungsten, molybdenum or palladium) having a pore volume of 15-20%, containing PdB (containing 27 atom % B) were heated at a temperature of $700^\circ C$. This heating operation caused the B_2O_3 formed to
- 10 spread across the surface of the wear-resistant material. Then this surface of the tool was contacted at $700^\circ C$ for 20 seconds with glass and thereafter the contact was broken. The fracture was located in the molten oxide layer.

15 CLAIMS

1. A method of handling or shaping glass at viscosities in the range from 10 to 10^9 Pa.s (10^2 to 10^{10} poises) with the aid of a tool comprising at least in a surface layer at all areas in contact with the glass a
- 20 boron-containing material which is a boride containing at least 5 atom % boron, boron carbide, or a boron-containing alloy containing at least 5 atom % boron.

2. A method as claimed in Claim 1, wherein the
- 25 said surface layer of the tool is coated with a layer of an inert material through which boron from the boron material can preferentially diffuse.

3. A method as claimed in Claim 1 or Claim 2, wherein at least the said surface layer of the said tool
- 30 consists of a wear-resistant, porous material, and the pores of this surface layer contain the boron-containing material or the B_2O_3 formed therefrom.

4. A method as claimed in Claim 1, substantially as herein described with reference to Example 1.

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