

PATENT SPECIFICATION

(11) 1 215 954

DRAWINGS ATTACHED

- (21) Application No. 58706/67 (22) Filed 27 Dec. 1967
(31) Convention Application No. W43078 VIb/32a
(32) Filed 28 Dec. 1966 in
(33) Germany (DT)
(45) Complete Specification published 16 Dec. 1970
(51) International Classification C 03 b 27/00
(52) Index at acceptance C1M 1P 1Q S16 S27A



(54) PROCESS FOR PRODUCING PRESTRESSED GLASS

(71) I, ERWIN WILHELM WARTENBERG, a German Citizen, of 213A, Birkenwaldstrasse, 7000 Stuttgart, Germany, do hereby declare the invention, for which I pray that a patent may be granted to me, 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 process for production of toughened glass by quenching a heated glass unit in a bath of chilling liquid.

It is known that increased mechanical strength may be imparted to glass by the process of toughening. Toughening is accomplished by heating of the glass and by subsequent, even and sudden cooling, referred to as quenching, chilling or tempering. Gases or liquids are employed as cooling fluids. Toughened glass is employed for example in the form of panes in self-propelled vehicles, because in addition to increased strength, it also has the property of safety fracture, i.e. the toughened glass panes fragmentate under impact stress into small particles, which do not as a rule have any sharp edges to cause injury and are not therefore dangerous.

With the liquid quenching processes known hitherto, it is possible to prestress glass of a thickness exceeding approximately 3.4 mms in such manner, that it has the property of safety fracture, together with increased mechanical strength. Whereas safety glass of a thickness between 5 and 6 mms has been employed hitherto for use on self-propelled vehicles, endeavours have been made to use safety glass of considerably lesser thickness, in order to save as much on weight of glass as possible in view of the ever increasing glass surface in proportion to the total area of the coachwork in accordance with modern styling.

Numerous attempts have been made to produce extremely thin glass suitable for application in automobile engineering having the desired mechanical as well as safety fracture properties, the thicknesses aimed at lying between 1.6 and 2.5 mms. No success has been achieved however hitherto in toughening glass of such small thickness

using the conventional quenching processes in such manner as to comply with the requirements specified by the automobile industry and by official safety regulations.

By a process based on the principle of ion exchange, which has recently become known, it may well be possible to produce glass of a thickness between 2.0 and 2.5 mms, possessing high mechanical strength and the required fragmentation or fracture pattern on shattering. Although the grades of glass produced according to this process may be thinner and have higher tensile strength than the grades of glass produced by the conventional toughening methods, the ion exchange process nevertheless has the great disadvantage that it is not applicable to standard plate or sheet glass (soda - lime - silica glass). On the contrary, aluminium - silicate glass must be used as an initial material in the ion exchange process, in order to engender a residual compressive stress in the surface of the glass by exchange of sodium for lithium ions. Owing to its chemical composition, standard grade plate or sheet glass is not suitable for an ion exchange of this nature and the chemical and physical changes connected therewith.

The present invention is thus concerned with the conventional toughening process referred to previously, in which the desired improvement is obtained by heating and rapid cooling of the glass. The invention is generally applicable to any conventional glass or glass form e.g. standard grade plate or sheet glass, and results in the production of toughened glass which, regardless of thickness, and in particular at smaller thicknesses than 3.5 mms, has approximately the same strength as the aluminium - silicate glass chemically toughened by ion exchange and referred to above, and on disintegration although its thickness may be as low as 0.8 mms, fragmentates into small particles which are not dangerous.

Toughened glass produced according to the invention is particularly appropriate for application in the form of a single sheet of safety glass in self-propelled vehicles. Its mechanical strength is approximately eight

times as great as that of untoughened glass and three times as high as that of glass toughened by quenching using hitherto conventional methods.

The invention provides a process for the production of toughened glass in which glass at a temperature near to its softening point is quenched in a chilling liquid which comprises a high boiling point carrying liquid with up to 4% by weight of a low boiling point liquid whose boiling point is at least 100°C below the boiling point of the carrying liquid.

By virtue of the considerable dilution of the low boiling point liquid by the carrying liquid, the low boiling point liquid may well vaporise in contact with the glass surface, but without resulting in the formation of a cohesive gaseous phase on the glass surface which occurred in the quenching processes employed hitherto, and was undesirable in so far as it prevented the very rapid cooling of the glass which is found to be necessary to attain a high degree of toughening in this type of glass.

In order that the invention may be more clearly understood some embodiments thereof will now be described with reference to the accompanying drawings, in which:—

Figure 1 shows a graphical illustration of the relationship between heat of vaporisation and the specific fragmentation number for different low boiling point liquids in different concentrations;

Figure 2 shows a graphical illustration of the relationship between concentration and specific fragmentation number of two different low boiling point liquids; and

Figure 3 shows graphically the dependence of the specific fragmentation number on the concentration of a particular low boiling point liquid.

A piece of plate glass of a thickness of e.g. 1.8 mm and having a coefficient of expansion of $90 \times 10^{-7} \text{ } ^\circ\text{C}^{-1}$, heated almost to softening point (e.g. to approximately 630°C in the case of particular plate glass grades), is quenched in pure boiling carbon tetrachloride (CCl_4), the continuous gaseous phase accompanying the cooling action has a duration of approximately 40 secs. A piece of glass toughened in this manner has a strength which is approximately doubled in comparison with untoughened glass. The glass does not however shatter into fragments and is therefore unsuitable as a safety glass.

An effective means of preventing the formation and persistence of a gaseous envelope consists of incorporating small quantities of a low boiling point liquid in a carrying liquid whose boiling range begins at 300°C, and of employing this mixture of liquids as a chilling liquid in a bath, for example at a temperature which lies close to the boiling point of the low boiling point

liquid. To this end, the boiling point of the carrying liquid should be at least 100°C above the boiling point of the low boiling point liquid so that practically no carrying liquid vaporises during the quenching action. At sufficiently low concentration of the low boiling point liquid, the carrying liquid in fact prevents the formation of a continuous gaseous phase, so that the cooling action occurs directly on the glass surface, and low boiling point liquid is vaporised. To establish a high degree of toughening, it is of importance to pass as quickly as possible through the temperature range from the softening point (e.g. 630°C) of the glass, to below the strain point, e.g. down to 350°C. The boiling action occurring on the glass surface is responsible for rapid passage through this temperature range. Further cooling from approximately 350°C to the temperature of the bath then has no effect on the toughening of the glass.

Figure 1 shows the relationship between the heat vaporisation and the specific fragmentation number for different substances employed as low boiling point liquid, for two different concentrations. It is apparent from Figure 1 that with increasing heat of vaporisation of the low boiling point liquid, the specific fragmentation number and thus the degree of toughening of the glass treated, also increases.

When 0.2% to 1% by weight of carbon tetrachloride is added to a mineral oil whose boiling range starts at approximately 300°C, and the mixture is heated to 80°C to 100°C and the hot mixture employed as a chilling bath for quenching glass 1.8 mm thick, by heating and then quenching the glass in the bath in conventional manner, toughened glass is produced which has a fragmentation number between approximately 15 and 45 per cm^2 , and a tensile strength of approximately 1,000 to 2,000 kgs/cm^2 or more. The results of such quenching tests are illustrated in Figure 2. As apparent from this figure, the fragmentation number and thus the tensile strength rise with increasing addition of carbon tetrachloride. The same tests, in which methanol (CH_3OH) is employed instead of carbon tetrachloride, give the curve illustrated at the right in Figure 2.

A greater addition than approximately 4% by weight of low boiling point liquid to the carrying liquid is not desirable since the tensile strength obtained rises no further or may even diminish again. It is apparent from Figure 3, that when carbon tetrachloride is employed as the low boiling point liquid, the fragmentation number obtained, which is proportional to the tensile strength, no longer increases appreciably above a concentration of about 1.5% by weight. Grooves and hair cracks damaging the glass surface may moreover occur during the quenching action,

if the low boiling point liquid is employed in excessive concentrations.

All organic and inorganic liquids which have a high boiling point, and which are difficult to vaporise and do not display any affinity to the glass, are suitable in principle as a carrying liquid, for example oils, particularly those having boiling points about 300°C and above, waxes, compounds with condensed benzene rings, e.g. such as terphenyl, and paraffins. Selection of the carrying liquid is of subordinate importance for the rate of cooling and thus the degree of toughening of the glass, since the greater proportion of heat transfer occurs by virtue of the vaporisation of the low boiling point liquid.

The low boiling point liquid is preferably one whose heat of vaporisation is more than about 40 cal/g. Suitable cooling liquids are carbon tetrachloride and methanol.

The fact that the rapid cooling of the glass accomplished according to the invention is caused by vaporisation of the low boiling point liquid present at low concentration in the carrying liquid, can be proved by the fact that with an identical carrying liquid and addition of equal concentrations of low boiling point liquids having different heats of vaporisation (see Figure 1) it is demonstrated that with increasing heat of vaporisation of the low boiling point liquid contained in the carrying liquid, the rate of cooling of the glass is increased, and thus its fragmentation number and mechanical strength.

If substances containing —OH groups and having a high heat vaporisation, e.g. alcohols such as methanol are employed in the chilling liquid, the glass grades obtained possess tensile strengths of approximately 3000 kgs/cm², thus considerably exceeding the tensile strengths of approximately 1000 kgs/cm² attainable according to the conventional toughening methods and coming close to the values typical for the grades of glass toughened by the ion exchange method. The fragmentation numbers attainable by the method according to the invention may amount to more than 100 per cm² with grades of glass of a thickness of approximately 1.5 mms. The mechanical stability of such thin glasses makes them extraordinarily pliable, so that they may be produced in the form of flat panes and may subsequently be installed with a certain degree of curvature in rigid curved mountings. The process of the invention is also applicable to hollow glass ware. Owing to the extremely short cooling periods, the process suggested is particularly appropriate for types of glass having low coefficients of expansion.

A decisive advantage of the process according to the invention moreover resides in that a specific fragmentation number or degree of toughening may be established

precisely by varying the percentage composition of the low boiling point liquid.

If the inventive process is applied on a larger scale, it is advisable to effect continual replacement of the low boiling point liquid vaporised by the cooling of the glass as it is quenched. This may occur either by condensation, e.g. by means of cooling coils, or by replenishment in the quantity corresponding to vaporisation, for example by continually feeding fresh liquid.

The cooling action obtained according to the invention is based on the vaporisation of the low boiling point liquid present in the carrying liquid in small concentration. Instead of vaporisation, rapid heat extraction by the cooling liquid may also occur by chemical decomposition or chemical transformation of the low boiling point liquid, so that all energy consuming processes in which the glass is rapidly cooled when it enters the chilling liquid can be effective in producing the required degree of toughening of the glass.

The process of the invention is illustrated further with reference to the following Examples:

Example 1

A plate glass sheet having a coefficient of expansion of $90 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$, of a size of 100×1.8 mms, is heated in an electrically heated furnace to approximately 630°C and immediately thereafter is immersed in a quenching bath situated below the furnace. The bath contains a mixture of 5 litres of a mineral oil heated to 100°C (density 0.91 g. cc⁻¹; viscosity 17.5 centistokes measured at 100°C; flashpoint 260°C) with 9 g. of carbon tetrachloride (= 0.2 weight %). The glass is cooled to a temperature of approximately 200°C within 6 secs, in this mixture. A fragmentation number of 8/cm² was determined after shattering.

Example 2

The procedure applied is that of Example 1, except that the concentration of carbon tetrachloride is raised to 0.5 weight % (= 22.5 g). After shattering the pane, a fragmentation number of 28/cm² was determined.

Example 3

The procedure of Example 1 is followed, with increase of the concentration of carbon tetrachloride to 1 weight % (= 45 g). After shattering the glass pane, a fragmentation number of 46/cm² was determined.

The results of Examples 1 to 3 are taken into account in the curve on the left-hand side of Figure 2.

Example 4.

The experiment described in Example 1 is repeated, but employing 0.1 weight % (= 4.5 g) of methanol instead of carbon tetrachloride. A fragmentation number of 32/cm² was determined.

Example 5

Compared to Example 4, the methanol concentration is raised to 0.5 weight % (= 22.5 g). The fragmentation number rises to 64/cm².

WHAT I CLAIM IS:—

1. A process for the production of toughened glass in which glass at a temperature near to its softening point is quenched in a chilling liquid which comprises a high boiling point carrying liquid with up to 4% by weight of a low boiling point liquid whose boiling point is at least 100°C below the boiling point of the carrying liquid.

2. A process according to Claim 1, wherein the temperature of the chilling liquid is maintained at about the boiling point of the low boiling point liquid.

3. A process according to Claim 1 or

Claim 2, wherein low boiling point liquid evaporated from the chilling liquid during quenching is replaced by being condensed or freshly added.

4. A process according to any one of Claims 1 to 3, wherein the carrying liquid is an oil whose boiling range begins at 300°C.

5. A process according to any one of Claims 1 to 4, wherein the low boiling point liquid is a liquid whose heat of vaporisation is more than 40 cal/g.

6. A process according to any one of Claims 1 to 5, wherein the low boiling point liquid is carbon tetrachloride or methanol.

7. A process for the production of toughened glass according to Claim 1, substantially as hereinbefore described with reference to the Examples.

8. Toughened glass produced by a process according to any one of the preceding claims.

PAGE, WHITE & FARRER,
Chartered Patent Agents,
27 Chancery Lane,
London, WC2A 1NT,
Agents for the Applicant.

Example 4

- 5 The experiment described in Example 1 is repeated, but employing 0.1 weight % (= 4.5 g) of methanol instead of carbon tetrachloride. A fragmentation number of 32/cm² was determined.

Example 5

- 10 Compared to Example 4, the methanol concentration is raised to 0.5 weight % (= 22.5 g). The fragmentation number rises to 64/cm².

WHAT I CLAIM IS:—

- 15 1. A process for the production of toughened glass in which glass at a temperature near to its softening point is quenched in a chilling liquid which comprises a high boiling point carrying liquid with up to 4% by weight of a low boiling point liquid whose boiling point is at least 100°C below the boiling point of the carrying liquid.
- 20 2. A process according to Claim 1, wherein the temperature of the chilling liquid is maintained at about the boiling point of the low boiling point liquid.
- 25 3. A process according to Claim 1 or

Claim 2, wherein low boiling point liquid evaporated from the chilling liquid during quenching is replaced by being condensed or freshly added.

4. A process according to any one of Claims 1 to 3, wherein the carrying liquid is an oil whose boiling range begins at 300°C. 30

5. A process according to any one of Claims 1 to 4, wherein the low boiling point liquid is a liquid whose heat of vaporisation is more than 40 cal/g. 35

6. A process according to any one of Claims 1 to 5, wherein the low boiling point liquid is carbon tetrachloride or methanol.

7. A process for the production of toughened glass according to Claim 1, substantially as hereinbefore described with reference to the Examples. 40

8. Toughened glass produced by a process according to any one of the preceding claims. 45

PAGE, WHITE & FARRER,
Chartered Patent Agents,
27 Chancery Lane,
London, WC2A 1NT,
Agents for the Applicant.

(7866) Printed by Her Majesty's Stationery Office Press, Edinburgh, 1970.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,
from which copies may be obtained.



* C L M S *