United States Patent

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[54] ION EXCHANGE STRENGTHENING OF GLASSES WITH LITHIUM VAPOR

11 Claims, 2 Drawing Figs.

[52] U.S. Cl. 65/30, 65/60, 117/106, 117/124
[51] Int. Cl. C03c 21/00
[50] Field of Search 65/30, 60, 114; 117/124, 106

[56] References Cited

UNITED STATES PATENTS

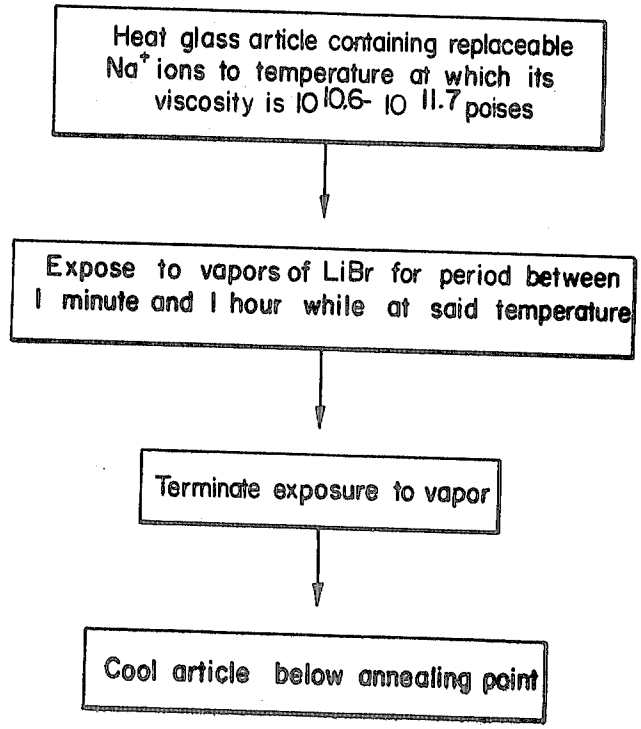
2,779,136 1/1957 Hood et al. 65/30

FOREIGN PATENTS

748,820 6/1962 Great Britain 65/30

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Assistant Examiner—John H. Harman
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ABSTRACT: Soda-lime glass articles are strengthened by exposure to vapors of certain lithium compounds while heated to or above the annealing point. Exposure at temperatures below the annealing point is avoided, to prevent etching the glass surface. Lithium ions migrate into a zone of the glassy network underlying the exposed surface and partially replace alkali metal ions therein. Upon cooling, the lithium-enriched shell is placed in compression about the glass article. Strength improvements are achieved in short periods of time.



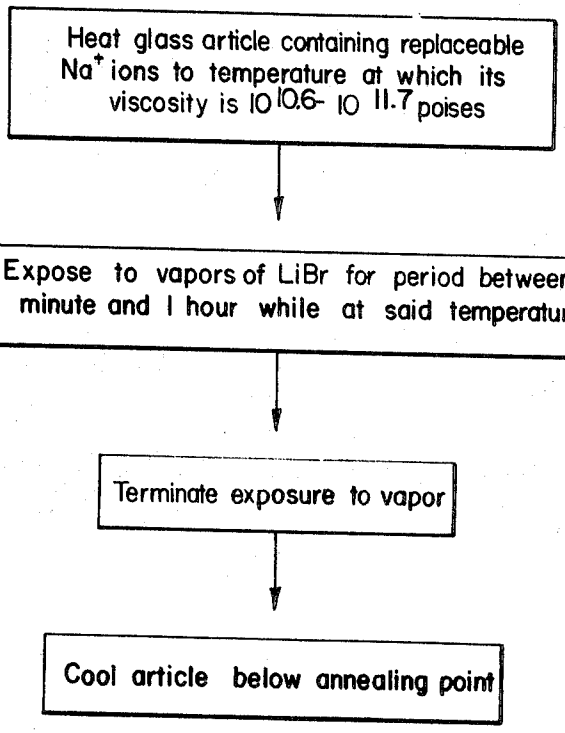


Fig. 1

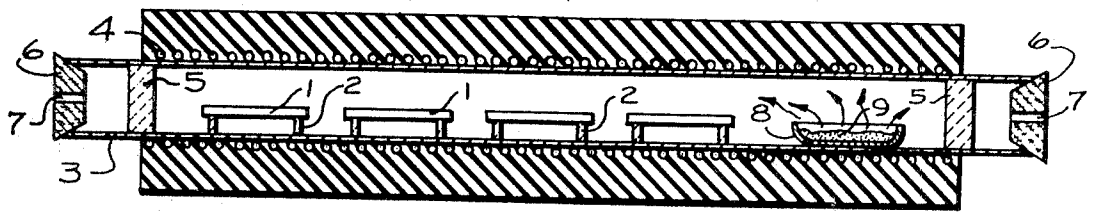


Fig. 2

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ION EXCHANGE STRENGTHENING OF GLASSES WITH LITHIUM VAPOR

This invention relates to a simplified method of strengthening glass articles by forming a compression shell in situ around the body of the article.

Various methods are known for strengthening glass articles by imparting or forming a compression layer on external surface areas of the article. One such method is tempering, wherein the heated article is quickly chilled so that the outside layer of the article is cooled and "shrinks" before the interior and is thereby placed in compression as the inside cools.

Another strengthening method involves the substitution or exchange, in a shallow surface layer, of smaller ions of an alkali metal from an external source, for larger alkali metal ions in the glass. In contrast to thermal tempering where the surface layer is placed in compression by differential cooling rates, in the ion exchange technique the surface layer is placed in compression around the interior of the body by reason of the fact that its composition is changed from that of the interior and its thermal contraction on cooling is less than the interior.

Stookey et al. U.S. Pat. No. 2,779,136 shows a prior method of strengthening by ion exchange. In that method the article to be strengthened is treated with a molten bath containing a lithium salt, and the smaller lithium ions are exchanged for the larger sodium ions in the glass surface.

Although high strengths can be achieved by the method of U.S. Pat. No. 2,779,136, it is a difficult if not impractical technique to apply in large-scale commercial practice because of the fact that it requires physically immersing the article in the molten salt bath. The cost of lithium salt is relatively high for the large baths required. Moreover the accumulation of sodium ions in the salt bath quickly reduces its utility, thereby requiring frequent replacement of the bath. The required immersion necessitates handling of each article at high temperature, and does not lend itself readily to treatment of hollow articles. The residue which adheres to the article upon its removal from the bath makes cleaning more difficult.

Perhaps the greatest difficulty with the previous lithium salt bath method is that the articles so treated are frequently clouded or frosted by contact with the liquid lithium compound, so that the article loses its clarity, thus rendering it useless for many purposes unless it is given special further polishing.

This invention is predicated upon the determination that the objectionable crazing or etching which was often incidental to the salt bath method of the prior art, can be avoided and other disadvantages of that method are obviated while still obtaining good strength increases in short treating times, if the article to be treated is exposed only to the vapors of certain lithium compounds, out of contact with any molten salt bath, and provided the vapor exposure is carried out only at temperatures above the annealing point of the glass.

In general, the lithium compounds utilized have very low vapor pressures and would not be expected to produce any effective strengthening by reason of the fact that the concentration of lithium ions in the vapor state adjacent the surface of the glass article is extremely small in relation to the level of concentration provided by a molten salt bath.

Nonetheless, I have found that it is possible to achieve strength improvements of as much as 150 percent, even by vapor treatments as short as 15 minutes. At the same time the clarity of the glass is preserved, and the clouding often caused by salt bath treatment is avoided.

The present invention can be used to treat articles of any glass composition which contains replaceable sodium and/or potassium ions. In broad terms, this includes glass compositions having about 7–25 total percent by weight of Na_2O and K_2O and about 45–80 percent SiO_2. The remainder may be constituted of other conventional glass-making compounds including CaO, Al_2O_3, MgO, ZnO, Li_2O, BaO, etc. Included in this group are the common soda-lime glasses of which containers and windows are ordinarily made and which comprise about 65–74 percent SiO_2, 14–17 percent Na_2O, 7–12 percent (MgO+CaO) and up to 3 percent Al_2O_3. Potassium oxide-containing glasses are much less important commercially than soda-lime glasses, but can also be treated by the method of this invention. The presence of more than about 5 percent B_2O_3 in the composition tends to reduce the replaceability of the sodium or potassium which is present.

The article to be treated can be of virtually any form, including both narrow-necked and wide-necked containers, sheet glass, molded or blown shapes, fibers and so on.

The lithium compounds which are useful herein are those which will volatilize without substantial decomposition or adverse reaction under treating conditions, and which can supply lithium ions (Li^+) to the glass surface. These include the halides, that is, lithium bromide, lithium chloride, lithium iodide and lithium fluoride. Other salts such as lithium sulfate can also be used, alone or in mixture with a lithium halide. Lithium amide, $LiNH_2$, is useful in the absence of water vapor and oxygen but tends to form lithium hydroxide, LiOH, in the presence of water vapor, which cannot be used in the method of this invention. The melting points and comparative vapor pressures of some of these compounds are as follows:

	Melting Point	1 mm. Pressure	10 mm. Pressure
LiI	835° F.	1,333° F.	1,546° F.
LiBr	1,017	1,378	1,630
LiCl	1,137	1,441	1,710
LiF	1,547	1,917	2,212

Lithium vapors can be generated directly in the treating chamber, for example from a crucible or shallow pan of the powdered material. Alternatively the vapors can be generated in a separate chamber and ducted into the treating chamber. To establish a more uniform vapor concentration it may be useful to employ a circulating fan. Where the inside of a hollow object is to be treated, means such as a nozzle can advantageously be used to establish more adequate exposure of such surfaces.

Broadly stated, the method according to this invention comprises forming an article of a glass composition containing replaceable sodium or potassium ions, heating the article to a temperature at or preferably above its annealing point, exposing it to vapors of the lithium compound for a period of time sufficient to permit a portion of the sodium and potassium ions adjacent the surface of the glass article to be replaced by lithium ions from the vapor, the exposure being carried out essentially only during the time when the article is above its annealing point, then cooling the article, the cooling from the annealing point to below about 800° F. being carried out in the absence of such vapor. The peak temperature of the heating cycle should not be so high as to cause undesirable deformation of the article.

I have found that it is important that the article be substantially exposed to lithium vapors only while heated to temperatures at or above its annealing point. That is, the article should be heated to and cooled from the treating temperature in the substantial absence of lithium vapors. Exposure of the article to lithium vapors while heated, but below the annealing point, tends to cause surface clouding. This effect is especially severe at temperatures between about 80° F. and the annealing point. However, such surface clouding or loss of transparency does not take place if the article is exposed to vapor of the lithium compound only at temperatures at or above the annealing point.

Under such proper exposure conditions, the products treated by this method display essentially the same transparency after strengthening as they displayed before it, and no clouding of the surface is manifest.

I have further found that exposure times between 1 minute and 1 hour at temperatures corresponding to glass viscosities of about $10^{10.0}$–$10^{12.6}$ poises are the most useful.

The term "annealing point," as used herein, has been defined by the American Society for Testing Materials as that temperature at which the glass article has a viscosity of 10^{13} poises. The annealing point can be determined by the method of ASTM C336–54I, as described in *A.S.T.M. Standards on Glass and Glass Products*, "Methods of Testing Specifications," 5th Ed., Dec. 1962.

If a glass article containing replaceable sodium or potassium is heated in the presence of lithium vapors of the type described, lithium ions will migrate from the surface of the glass into the interior, displacing or replacing sodium and/or potassium ions therein. Displacement of sodium ions, for example, by this process can readily be detected by the formation of a film of the corresponding sodium salt on the surface of the article. The presence of exchanged lithium can be confirmed by chemical analyses performed on glass dissolved from a thin layer of the treated surface.

The following glass compositions, in parts by weight as analyzed, are illustrative of various types of glasses which can be used in carrying out the new method.

COMPOSITION

Oxide	A	B	C
SiO_2	67.9	73.0	55.2
Na_2O	15.8	14.4	18.3
2O	0.5	0.1	4.1
$2O_3$	2.9	1.4	21.6
B_2O_3	1.7		
Fe_2O_3	0.04	0.03	0.07
BaO	2.1		
CaO	5.5	6.8	0.6
MgO	3.8	4.3	0.09
Li_2O	trace		
TiO_2	0.02		
MnO		0.003	
SO_3	0.3	0.02*	
Annealing point, °F.	972	1,007	1,080

Expressed as S

Compositions A and B are typical soda-lime types of glasses while composition C is a high sodium-aluminum silicate glass.

In the drawing, FIG. 1 is a flow sheet showing a preferred method of carrying out the new method and FIG. 2 is a diagrammatic section of apparatus useful for carrying out the method on a batch basis.

EXAMPLE 1

Glass rods 1 of composition A, of very uniform cross section, were placed on a refractory support 2 in a horizontally mounted tube 3 as shown in FIG. 2. The glass rods 1 were positioned at different axial positions along the length of the tube, as shown. The tube 3 was heated externally by resistive coils 4 along its length. The ends of tube 3 were closed by refractory plugs 5 and stoppers 6. The tube 3 and rods 1 therein were heated in air to approximately 1,100° F., corresponding to a viscosity of the glass of composition A of about $10^{10.6}$ poises. A small hole 7 in each stopper 6 permitted atmospheric pressure to be maintained in the tube 3. A porcelain boat 8 containing powdered lithium bromide (LiBr) 9 was separately preheated to 1,100° F. and when it had reached that temperature, was placed into one end of the tube 3. The LiBr 9 volatilized from the boat 8 and permeated the interior of the tube 3. Molecules of vaporized LiBr came into contact with the surface of the rods 1 and a portion of the lithium, believed to be in the ionic state, migrated from the surface into the glass network in a zone underlying the surface, displacing sodium therein.

The furnace was held at 1,100° F. for 15 minutes with the source of LiBr in place, after which the boat 8 was removed. The rods were cooled to below 700° F. over a period of about 20 minutes. A white powdery film was visible on the surface of the glass rods upon their removal from the treating furnace. The film was completely removable by rinsing with water, and upon analysis was identified as NaBr. This is an indication that lithium ions diffused into the surface zone and replaced a proportion of the sodium therein and that the displaced sodium ions recombined with bromide anions on the surface of the glass to form the sodium bromide film. The glass rods were clear (uncolored) and the lithium enrichment of the surface imparted no visually detectable color, either as viewed in the direction perpendicular to the surface or parallel to the surface.

The surface of the rods was not etched or crazed and displayed no clouding of the type frequently found on the surface of rods which are treated in molten lithium salt. For example, if rods of this same composition are treated in a molten lithium bromide bath for 15 minutes at 1,100° F., etching is manifest which would render the rods useless for most purposes, without special polishing. Even the presence on the article during cooling in air of a lithium salt film from a molten treating bath can cause etching.

After cooling and rinsing, the rods were tested for abraded strength. This test procedure was carried out by placing the rods in a jar containing 150-mesh silicon carbide. The jar was rotated at 100 r.p.m. on a ball mill rack for 5 minutes. The rods were stressed by applying load at the center of a 2-inch span and increasing the load at a rate of about 8 pounds per second until fracture occurred. The approximate strengths of the rods in p.s.i., as calculated from their cross section, ranged between 26,100 and 51,300 p.s.i., and varied with the LiBr concentration along the tube.

The abraded strength of untreated glass rods of the same composition was about 20,000 p.s.i. Thus, the LiBr treatment effected strength increases of about 30 to 150 percent as compared to the controls. Rods given a similar thermal cycle in the absence of LiBr vapor quickly abrade to their initial strength.

EXAMPLE 2

Glass rods of composition A, approximately 3/16 inch × 4½ inches, were placed in a stainless steel vessel or chamber about 8 inches high, 10 inches wide, and 11 inches long. Powdered LiCl was spread in a uniform layer about ¼-inch deep over the bottom of the chamber. The glass rods to be treated were supported on refractory bars in the chamber. The chamber was placed in a gas fired circulating atmosphere furnace. Circulation rapidly swept the vapor from the chamber, so that essentially no lithium vapor collected in the chamber until a cover or lid was placed on it.

The furnace was heated from room temperature to 1,130° F., and the cover was then placed on the chamber to concentrate the LiCl vapor in it. After a 1 hour exposure period the cover was removed from the chamber to effectively terminate the exposure, and the furnace was permitted to cool at its natural rate over a period of about 1 hour, at which time the rods were removed. After removal of a powdery NaCl film, the rods were found not to be clouded, etched or crazed by their exposure to the vapor. The average strength of the rods so treated was found to be about 29,000 p.s.i. Longer abrading of both the controls and the treated rods causes a much greater differential between the comparative strengths.

The calculated vapor pressures of the lithium halides at 1,100° F. are very low, as apparent from the following tabulation:

LiBr	0.063	mm Hg
LiI	0.058	mm Hg
LiCl	0.026	mm Hg
LiF	0.00003	mm Hg

this is reflected by the generally higher strengths achieved at equivalent and even at reduced treating times with LiBr as compared to LiCl and LiF.

EXAMPLE 3

Glass rods of composition A were treated with LiCl in the chamber specified in example 2. The rods were heated to

1,100° F., and four crucibles containing powdered LiCl were then placed in the chamber and the lid was closed. The rods were exposed for 1 hour after which the crucibles were removed and the rods cooled out of substantial contact with LiCl.

The rods so treated had a visible, white, easily removable sodium chloride film on the surface, but after removal of the film were transparent and were not etched or crazed by the vapor treatment. They had an average abraded strength of 24,800 p.s.i., as compared to 18,600 p.s.i. for an untreated standard at the same abrasion conditions.

EXAMPLE 4

Glass rods of composition A were placed in a chamber about 4½ inches high, 10 inches wide and 11 inches long. The rods were supported on refractory bars about 1½ inches above the bottom of the chamber. Two crucibles filled with powdered lithium fluoride were placed in the treating chamber. The exposed surface of the LiF in the crucibles was a circle about 1¼ inches in diameter and was about one-half inch from the crucible rim. The chamber was closed and placed in a furnace with a very rapid heat-up rate. With both the rods and crucibles in place, the furnace was heated to about 1,100° F. at rate of about 3,000° F. per hour, and was held at 1,100° F. for 1 hour. The rods so treated had an average strength of 25,000 p.s.i. compared to the standard rods with average strength of 20,000 p.s.i., and were free from clouding.

Examples 2–4 demonstrate that where the heat-up rate is very rapid so that there is only brief exposure of the articles to the lithium vapor at temperatures above about 800° F. but below the annealing point, or where the concentration of the vapor is very low during that range of heating, such insubstantial exposure, even though it is below the annealing point, does not cause clouding. However, if the rods were exposed to more concentrated vapors over a gradual heat-up, the danger of etching or clouding is significant.

EXAMPLE 5

Lithium amide, $LiNH_2$, has a high vapor pressure but tends to form lithium hydroxide and ammonia in the presence of water vapor:

$$LiNH_2+H_2O \rightarrow Li(OH)+NH_3$$

Under such conditions the amide is not generally useful according to the method of this invention. However, I have found that the amide can be used in the substantial absence of water. This is demonstrated by a test in which rods of composition A were placed in a tube furnace and exposed to $LiHG_2$ vapors at 1,100° F. for 10 minutes while dry nitrogen was passed through the tube to sweep out any water vapor. Upon cooling, the rods so treated were unclouded and displayed an average tensile strength of about 33,500 p.s.i. The rods were free from etching, although they had a noticeable brownish coloration.

EXAMPLE 6

Like the lithium halides, lithium sulfate can be used in an ordinary atmosphere, and it shows no tendency to color the rods. Moreover, I have found that it effects unusually large strength improvements in short treating times.

Rods of composition A were placed in a tube furnace of the type described in example 1, and were heated to 1,100° F. in air. When the furnace reached 1,100° F., a boat containing Li_2SO_4, preheated to 1,100° F., was placed in the furnace. Temperature was held at 1,100° F. for 10 minutes, after which the boat was removed and the furnace was cooled. The rods displayed strengths of 42,300 p.s.i. and were free from staining or etching.

EXAMPLE 7

One convenient means of providing a large surface area of the lithium source is to saturate it into a porous refractory material. In this example, a porous insulating fire brick, 4½ inches × 9 inches × 1 inch standing on the 9 inches × 1 inch face, was saturated with 150 grams of lithium bromide. The brick and LiBr were individually preheated, and the LiBr was poured onto the brick while both were at the same temperature. The brick may then be cooled to room temperature before use.

Nonreturnable, clear beverage bottles of composition B were heated at 1,100° F. and the brick saturated with lithium bromide was placed in a furnace for 15 minutes at 1,100° F. The furnace was heated on all six sides to maintain even temperature conditions. The brick was then removed and the bottles were cooled in the furnace to room temperature.

Without treatment, these bottles had average internal breakage pressures of 366 p.s.i. as measured on a standard internal pressure tester. After treatment, two of the four bottles had average strengths in excess of the maximum 550 p.s.i. of which the tester was capable, a third broke at 550 p.s.i., and the fourth broke at the base contact point under a pressure of 375 p.s.i.

EXAMPLE 8

Bottles of composition B were treated according to the method described in example 7, except that the furnace was held at about the 1,007° F. annealing point of the bottles for 60 minutes. The average strength of these bottles was 425 p.s.i.

By way of comparison, when similar bottles were treated at 950° F. (below the annealing point) for a period of 45 minutes, their strength was actually reduced, to a level lower than that of the untreated bottles.

EXAMPLE 9

Soda-lime rods of composition A were heated to 1,100° F. A preheated brick saturated with LiBr was then placed in the furnace and the rods were exposed to the vapor for 15 minutes, at the end of which the brick was removed and the furnace cooled to room temperature. The average strength of the rods was 35,700 p.s.i.

EXAMPLE 10

The freedom from etching of glass articles treated in accordance with the method of this invention, in comparison to treatment at the same conditions with a molten salt bath, is illustrated by the following comparison: One end of a piece of ordinary soda-lime window glass was placed in a melt of LiBr at 1,150° F. for 30 minutes, then removed and cooled. The other end of the sample was out of contact with the molten salt, but was exposed to LiBr vaporized from the melt. The portion of the sample which had been in the melt was severely etched, but the upper portion was clear.

In articles treated by the method of this invention, the lithium ion-enriched surface layer is in compression. This can be ascertained by viewing a thin fractured sample edgewise in polarized light between crossed nicols in a microscope, according to known technique.

The presence of a visible white sodium or potassium salt film on the exposed surface of the treated articles can be taken as one convenient indication that the heating cycle has caused the lithium vapor to displace other alkali ions in the glass.

It is important, from the standpoint of achieving useful strength increases at rapid rates, that the lithium vapor concentration be as high as possible. To that end, subatmospheric pressures in the treating chamber can be used to increase the lithium ion concentration. Decreasing the distance from the emitting source to the ware also serves to enrich the vapor concentration at the glass surface.

The peak temperature at which any specific glass article can be most effectively treated depends upon the shape of the article. In general the article should not be treated at temperatures at which undesirable deformation or sagging out of the proper final shape occurs. Temperatures which are suitable

for articles of one particular shape may tend to cause undesirable sagging of larger, more complex, or more delicate shapes of the same glass composition. On the other hand, treatment at higher temperatures can be used for shapes where deformation is not a critical operating restriction, for example with sheet glass, or where deformation is needed to cause the article to sag into a desired final shape. Ordinarily treatment at viscosities in the range of $10^{10.0}$ to $10^{12.6}$ poises is the more suitable, and treatment at glass viscosities of about $10^{10.6}$ to $10^{11.7}$ poises is particularly useful because it appears to effect ion exchange in a relatively sharply defined layer. For soda-lime glasses, temperatures of about 25°–150° F. above the annealing point are suitable.

While the foregoing examples illustrate the preferred practice of this invention, it should be understood that I do not intend to be so limited, and that the invention also includes other embodiments and modifications falling within the scope of the claims which follow.

I claim:

1. A method of increasing the strength of a glass article made from a composition including 7–25 percent (Na^2O+K_2), 45–80 percent SiO_2, and not more than about 5 percent B_2O_3, said method comprising,

first heating the article to a temperature not lower than its annealing point, but below the temperature at which the article sags out of desired shape, in the absence of substantial amounts of lithium treating vapor,

subsequently exposing at least a portion of the surface of said article, while heated to said temperature, to vapor of at least one lithium compound selected from the class consisting of LiBr, LiCl, LiF, LiI, $LiNH_2$ in the absence of water, and Li_2SO_4, and continuing said exposure for a period of time sufficient to replace a portion of the alkali metal ions with lithium ions from said vapor,

and cooling said article below the annealing point the exposure to lithium vapor being prevented during cooling while said article is between the annealing point and about 800° F.

2. The method of claim 1 wherein said exposure is for a period between 1 minute and 1 hour.

3. The method of claim 1 wherein said exposure is carried out by placing a supply of said compound adjacent to said article in a furnace.

4. The method of claim 1 wherein said exposure is carried out at temperatures corresponding to glass viscosities of about $10^{10.0}$ to $10_{12.6}$ poises.

5. The method of claim 1 wherein said exposure is carried out at temperatures corresponding to glass viscosities of $10^{10.6}$ to $10^{11.7}$ poises.

6. The method of claim 1 wherein said composition is a soda-lime glass composition comprising about 65–74 percent SiO_2, 14–17 percent Na_2O, 7–12 percent (MgO+CaO), and up to 3 percent Al_2O_3.

7. The method of claim 1 wherein said exposure is carried out at a temperature of 25°–150° F. above the annealing point of said article.

8. A method for making a strengthened glass article comprising,

first, melting a batch of glass-making ingredients so as to provide a glass batch having on an oxide basis about 65–74 percent SiO_2, 14–17 percent Na_2O, 7–12 percent (MgO+CaO) and up to 3 percent Al_2O_3,

forming at least one article from said glass batch,

introducing said article into a treating chamber and heating it therein to a temperature above its annealing point but below the temperature at which the article sags out of desired shape, in the absence of substantial amounts of lithium treating vapor,

subsequently introducing into said chamber, while said article is at said temperature, a vapor of at least one lithium compound selected from the class consisting of LiBr, LiCl, LiF, LiI, $LiNH_2$ in the absence of water, and Li_2SO_4, and exposing at least a portion of the surface of said article to said vapor in said chamber at said temperature for a period of time between 1 minute and 1 hour sufficient to replace a portion of the alkali metal ions with lithium ions,

terminating the exposure of said article to said vapor,

then cooling said article from said temperature to room temperature in the absence of vapor.

9. The method of claim 8 wherein a supply of said compound is placed in the chamber adjacent said article.

10. The method of claim 9 wherein said supply is removed from said chamber before said article is cooled from said temperature.

11. The method of claim 9 wherein said supply is preheated to the temperature at which said article is to be exposed, before said source is placed in said chamber.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,615,319 Dated October 26, 1971

Inventor(s) Francis Joseph Shonebarger

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 63, "80° F." should be --800° F.--

Column 3, line 5, "C336-54I" should be --C336-54T--

Column 3, Composition Table, separating line should be under column titles

Column 3, Composition Table line 3, "20" should be --K_2O--

Column 3, Composition Table line 4, "20_3" should be --Al_2O_3--

Column 5, line 51, "$LiHG_2$" should be --$LiNH_2$--

Column 7, line 22, "$(NA^2O + K_2)$" should be --$(NA_2O + K_2O)$--

Column 8, line 2, "$10_{12.6}$" should be --$10^{12.6}$--

Signed and sealed this 18th day of April 1972.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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