

United States Patent

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2,622,016	12/1952	Gilstrap.....	156/24
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**[54] METHOD OF PRODUCING GLARE-REDUCING
GLASS SURFACE**
12 Claims, No Drawings

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156/24, 252/79.3, 65/31

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[50] **Field of Search**..... 156/24;
65/30, 31; 161/1; 252/79.3

[56] **References Cited**

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3,374,130	3/1968	Junge et al.....	156/24
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ABSTRACT: An improved glare-reducing glass surface is produced by including an undissolved inorganic salt of small crystal size, e.g., in the range of 10–50 microns in diameter and 2–10 micron in height, in the etching bath of an etching process. The etching process involves cleaning the glass surface, etching in a hydrofluoric acid bath or similar acid bath containing the undissolved salt by virtue of a saturated condition of the bath. Saturation of the bath is usually accomplished by ammonium bifluoride or other salt. After etching, the surface is properly polished and cleaned. The preferred, inorganic salt crystals are crystals of potassium bifluoride, sodium bifluoride, and calcium phosphate.

METHOD OF PRODUCING GLARE-REDUCING GLASS SURFACE

FIELD OF THE INVENTION

This invention relates to a new and improved method of etching a glass surface to produce glare-reducing glass.

DESCRIPTION OF THE PRIOR ART

Processes for producing glare-reducing glass have previously been proposed. An example of one such process which has been in commercial practice for a number of years is that disclosed by V. M. Gilstrap et al. in U.S. Pat. No. 2,622,016, entitled "Method of Producing Television Tube Face." According to that process, a glass surface is first cleaned with water and then dipped in three consecutive baths. The first bath is a cleaning and primary etching bath which is a water solution containing hydrofluoric acid, e.g., about 8 to 12 percent. The second bath is the etching bath which is a supersaturated solution of ammonium bifluoride, hydrofluoric acid and water. This bath can be prepared, for example, by mixing six pounds of technical grade ammonium bifluoride, one pound of chemical grade 52 percent hydrofluoric acid and four pounds of water, and can also contain small amounts of sodium chloride and diethylene glycol. After etching in the second bath, the glass surface is then dipped in a third hydrofluoric acid bath containing, for example, 15 percent to 35 percent by weight commercial 52 percent hydrofluoric acid, and the surface is then rinsed and dried to complete the etching process. Such a method provides a glare-reducing surface but the size of the protuberances of the etched surface has been found to be about 5-20 microns in height and 25-100 in diameter. Thus, the protuberances vary greatly in their sizes and decreasing this variance, as well as the actual protuberance size, would result in an improved and more uniform glare-reduced surface.

SUMMARY OF THE INVENTION

The size of the protuberances formed on a glass surface during etching of the glass can be significantly reduced by including in the etching bath an inorganic salt having a small ultimate or minimum crystal size which has a surface portion in the range of about 2 to 10 microns in height and 10 to 50 microns in diameter. During the etching process, the salt is contacted with the glass surface and causes the etching of a depression the size and shape of the crystal surface, thereby forming between the depressions nodular protuberances of small physical size, smaller than heretofore provided. A major proportion, i.e., over 50 percent, of these protuberances are in the range of 2 to 10 microns in height and 10 to 50 microns in diameter, generally about the same size and shape of the salt crystal, while the remaining protuberances can be larger. The resulting etched glass surface is uniform in the virtual absence of specular areas of reflection and the surface has markedly improved glare-reducing characteristics.

While this invention is susceptible of embodiment in many different forms, there will herein be described in detail an embodiment of the invention with the understanding that the present disclosure is to be considered as an exemplification of the principles of the present invention and is not intended to limit the invention to the embodiment described.

THEORY OF THE FUNCTION OF THE INORGANIC SALTS

The etching bath is an acid bath containing soluble salts which saturate the bath, usually with an excess of the soluble salt. Although the additional salts added to the bath according to the present invention may also be soluble, the saturated nature of the bath prohibits complete dissolution of such salts so that when the additional, small crystal salts are added to the bath, they resolve to an ultimate or minimum crystal size and agitation of the bath places these crystals in contact with the glass surface. It is believed that the crystals assist the etching

function of the acid bath in removing silica from the areas of contact with the glass surface to produce etched depressions in the glass which are images of the contacting crystal surface. The protuberances are thereby created between depressions. Because of the small crystal size, the protuberances are also of small size, e.g., about the same size as the crystals and these small size protuberances produce less specular reflections and optical confusion or sparkle when images are viewed through the treated glass. Further, the small size of the protuberances permits more uniformly sized protuberances over the glass surface resulting in more uniform glare-reducing properties.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The above identified U.S. Pat. No. 2,622,016 of Gilstrap et al. and all descriptive matter contained therein is incorporated herein by reference. According to the preferred embodiment of this invention, the method described in the Gilstrap et al. Patent is used with the modification disclosed herein.

In accordance with one embodiment of the present invention, the etching bath of prior processes is modified by the inclusion of salts having a small ultimate crystal size in the saturated etching bath. The salts are used in an amount in the range 0.1 to 20 and preferably 0.5 to 5 weight percent insoluble or undissolved crystals in the bath. Thus, where normally soluble salts are used in accordance with this invention, the salts can be used to saturate or help saturate the bath and an additional amount in the above ranges is included over and above that required for saturation. Usually a salt of larger ultimate crystal size such as ammonium bifluoride will be used to saturate the acid etching bath and the salt of the present invention will be added in a proper amount over and above the amount of larger crystal salt.

The useful salts have an ultimate crystal size falling in the range of 2-10 microns by 10-50 microns. Useful salts can be selected from the metal salts of mineral acids and preferably the metal bifluorides and phosphates such as sodium bifluoride, potassium bifluoride, calcium phosphate and the like. Usually the salts will be added as larger crystal pieces and will resolve to proper crystal size in the bath.

In the preferred process, the method of the above-identified Gilstrap et al. patent is further modified by omitting sodium chloride from the etching bath by using commercial 70 percent hydrofluoric acid in the final or polishing bath and by also using sulfuric acid in the polishing bath as a substitute for a portion of the hydrofluoric acid so as to conserve the amount of hydrofluoric acid used. The use of 70 percent hydrofluoric acid in the polishing bath materially reduces the time required for polishing the glass to a higher gloss reading which is now often required by purchasers of glare-reduced glass.

In a typical example of the etching method of this invention, glass articles, on which it is desired to provide glare-reducing surfaces, are treated in three stages as follows:

STAGE NO. 1

Etching the Surface

The glass sheets are loaded into a suitable rack that will support them throughout the baths used in the three stages. The rack is of an acid resistant material such as monel, hard rubber or polyvinylchloride and the glass sheets are supported in an upright position with about a 1-inch spacing between them. While in the rack the glass is first rinsed with water to remove residual material which may remain as a result of the glass manufacturing process. The rack, carrying the glass sheets, is then submerged into a chemical cleaning bath to clean grease and/or other acid resisting materials from the surface and prepare the surface for the etching solution. In this cleaning bath, some preliminary etching can occur. An example of a suitable cleaning bath solution is one containing from about 10 percent by weight of 70 percent of hydrofluoric acid, or the equivalent thereof in water. Preferably, the cleaning bath is agitated to facilitate the removal of deposits from the glass surface and the glass is maintained in this bath for a short

period of from, e.g., 1/2 minute to 2 minutes at ambient or slightly higher temperatures, e.g. 60°-95° F. The time of dipping in this bath is governed only by the cleaning of the glass surface. Such glass cleaning operations are conventional and many are known to the art and can be substituted for the cleaning operation described above.

After the glass is removed from the cleaning bath, it is submerged in the etching bath for the purpose of roughening the surface of the glass to give the glass surface a frosty appearance. The etching bath, in accordance with this invention, includes an inorganic salt crystal as previously described. A suitable bath can contain the following ingredients in the following amounts:

Ammonium bifluoride crystals	10 to 50 parts and preferably 20 to 40 parts by weight
Hydrofluoric acid (based on 70% HF)	1 to 20 parts and preferably 5 to 10 parts by weight HF)
Potassium Fluoride	0.1 to 20 parts and preferably 0.5 to 5 parts by weight
Diethylene glycol	0 to 50 parts and preferably 20 to 30 parts by weight
Water	10 to 50 parts and preferably 25 to 45 parts by weight

Other inorganic salts such as sodium bifluoride or calcium phosphate can be substituted for the potassium bifluoride. The diethylene glycol, or other soluble or miscible organic liquid, preferably a polyol, assists in controlling the uniformity of the etched frost of the surface. Suitable substitutes for diethylene glycol include ethylene glycol, propylene glycol, glycerine, sorbitol, corn syrup, pentaerythritol trimethylol propane or the like.

The glass is maintained in the etching bath while agitating the bath for a short period of time until the desired appearance of frost is obtained. This will usually require from about 1/2 to 2 minutes at a bath temperature at or slightly above ambient temperature, e.g. 65°-95° F. Of course, higher temperatures can be used to decrease the etch time and at lower temperatures longer etch times may be required.

STAGE NO. 2

Reetching of the Surface

The glass is resubmerged into the cleaning solution in the manner as discussed above and all stages are repeated through removal of the glass from the etching bath. This results in reetching the glass surface. It has been found that in the initial etching dip, insoluble salts form on the glass surface and the etching action is thereby slowed and eventually becomes ineffective. Returning the glass to the cleaning solution removes these deposits and produces a clean surface so that the etching process can continue at a faster rate. The reetching permits the complete surface to be attacked by the bath, thereby further assuring elimination of untreated surfaces which may produce specular reflections. After the reetching, the glass is obscure and completely frosted or etched.

The surface can be examined, if desired, through a measuring microscope to verify that the etched nodular protuberances are of the desired size. If etching is incomplete, the glass can be returned to the etching bath as often as necessary.

STAGE NO. 3

Polishing the Reetched Surface

After removal of the glass from the etching bath in the reetching stage, the glass is treated to remove all residual water, e.g., by forcing heated air over the surface of the glass. The dried glass is then submerged into a polishing bath for the purpose of modifying or even eliminating the frosty appearance and for the further purpose of polishing the glass to return it toward its original transparent state. A suitable

polishing bath can consist of 20-40 percent by volume of 70 percent hydrofluoric acid, 20-40 percent by volume of sulfuric acid (66° B.), and the remainder of water. Higher acid concentration results in faster polishing action while lower acid concentrates slows the polishing action. Usually the polishing bath will be at ambient temperatures or above, e.g., 65°-120° F. and the polishing time is decreased at the higher bath temperatures. The glass should be polished until the desired gloss is attained, e.g., as measured with a Gardner gloss meter.

After removal from the polishing bath, the glass is submerged in a water bath to stop the polishing action of the polishing bath acids. The glass is then rinsed to remove all residual acids and is dried and then inspected to determine that the glass meets the specifications required. The glass now has a uniformly treated surface that will reduce the reflected light resulting from light striking the surface and which also will not affect the ability to resolve images through the glass by light transmitted.

In one example of the invention, the above typical method was carried out on a series of glass sheets using a cleaning solution of 8 percent of 70 percent by weight hydrofluoric acid in water, an etching bath containing 30 percent by weight ammonium bifluoride crystals, 8 percent by weight hydrofluoric acid, X 3 percent by weight potassium bifluoride, 25 percent by weight diethylene glycol and the remainder water, and a polishing bath containing 30 percent by volume 70 percent hydrofluoric acid, 30 percent by volume sulfuric acid (66° B.) and the remainder water. The baths were at normal operating temperatures for ambient conditions and no external heat was applied so the baths were usually slightly above ambient temperatures due to heat created during the process. The glass sheets treated in this process all had excellent glare-reduced surfaces with Gardner gloss meter readings in the range of 60-70 at a 60° angle with a large aperture; this compares with readings of only 35 to 45 from prior process not utilizing the small crystal salts. The nodular protuberances of the resulting etched surfaces were of small size with the majority, e.g., over 50 percent, falling in the range of 2-10 microns in height and 10-50 microns in diameter.

The example is repeated using sodium bifluoride or calcium phosphate in lieu of the potassium bifluoride and similar results are obtained.

I claim:

1. In a method for etching glass surfaces containing silica for producing glare-reduced glass wherein the glass is subjected to etching involving the action of a hydrofluoric acid etching bath saturated with a relatively large crystal salt having a crystal size for normally producing protuberances on the glass surface 5-20 microns in height and 25-100 microns in diameter and comprising ammonium bifluoride, the improvement which comprises including in said bath from about 0.1 to about 20 weight percent of an inorganic salt having an ultimate crystal size in the range of about 2-10 microns in height and about 10-50 microns in diameter and selected from the class consisting of sodium bifluoride, potassium bifluoride and calcium phosphate.

2. The method of claim 1 wherein said amount of the smaller crystal size salt is in the range of 0.5 to 5 weight percent.

3. The method of claim 1 wherein said smaller crystal salt is potassium bifluoride.

4. In a method for etching glass surfaces containing silica for producing glare-reduced glass wherein the glass is subjected to etching involving the action of a hydrofluoric acid etching bath saturated with a relatively large crystal salt having a crystal size for normally producing protuberances on the glass surface 5-20 microns in height and 25-100 microns in diameter and comprising ammonium bifluoride, the improvement which comprises including in said bath from about 0.1 to about 20 weight percent of an inorganic salt having an ultimate crystal size in the range of about 2-10 microns in height and about 10-50 microns in diameter and selected from the

class consisting of sodium bifluoride, potassium bifluoride and calcium phosphate, said etching bath comprising 1-20 weight percent hydrofluoric acid (based on 70 percent HF), 10-50 weight percent bifluoride crystals, 0-50 weight percent diethylene glycol, 10-50 weight percent water, and 0.1-20 weight percent potassium bifluoride.

5 5. The method of claim 4 wherein the weight percents of said five ingredients are seriatim 5-10, 20-40, 20-30, 25-45 and 0.5-5.

6. The method of claim 1 wherein said cleaning operation comprises washing the glass surface with dilute hydrofluoric acid.

7. The method of claim 1 wherein said polishing operation comprises dipping the glass recovered from the etching bath into a polishing bath comprising an aqueous hydrofluoric acid and sulfuric acid bath.

8. The method of claim 7 including the step of rinsing the glass after recovery from the polishing bath.

9. The method of claim 1 wherein said etching operation is repeated at least once until the protuberances of the desired size, over 50 percent of the protuberances having a height in the range of 2 to 10 microns and a diameter in the range of 10 to 50 microns, are formed uniformly over the glass surface.

10. A substantially nonreflective transparent article made by the method of claim 1 and comprising a body of glass having a glare-reduced, etched and polished surface defined by protuberances of glass at said surface.

11. The article of claim 10 wherein said protuberances are defined by depressions of silica removal from a smooth glass surface, said depressions being the general size and shape of inorganic salt crystal surface portions having a height and diameter in said restrictive ranges.

12. The article of claim 10 wherein a major amount of the protuberances have a height in the range of 2-10 microns and a diameter in the range of 10-50 microns.

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