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(54) **Method of Applying Electrically Conducting SnO<sub>2</sub> Layers on Alkali-Rich Glass**

(57) An unclouded, electrically conductive SnO<sub>2</sub> layer is formed on an alkali-rich glass in an economic

manner in a continuous process. By spraying a solution of dialkyl tin oxide onto the heated glass and immediately after this and without reheating the glass a solution of SbCl<sub>4</sub> and HF in an organic solvent is sprayed onto the applied SnO<sub>2</sub> layer.

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## SPECIFICATION

**Method of Applying Electrically Conducting SnO<sub>2</sub> Layers on Alkali-Rich Glass**

This invention relates to a method of applying electrically conducting SnO<sub>2</sub> layers on alkali-rich glass.

The expression "alkali-rich glass" is first and foremost used to describe float glass or a type of glass made by a process other than the float process but having similar Na content to float glass. The preferred method of applying electrically conducting SnO<sub>2</sub> layers is by spraying. This involves spraying a sheet of glass at 600°C with SnCl<sub>4</sub> in a solvent together with hydrofluoric acid to form a layer of SnO<sub>2</sub> doped with fluorine on the glass. The resulting layers have ohmic resistances of 10—30Ω/□ or more and IR reflections of 80 to 70% or less. The layer is completely unclouded on glass substrates which have a low alkaline content such as, e.g. Tempax glass (made by Schott) which contains ~4% alkali. However, on an alkali-rich glass of the float glass type, comprising ~12% alkali, a clouded layer will form. The clouding effect caused by a reaction of the Na in the glass with the Cl<sup>-</sup> of the spraying solution to form sodium chloride.

Now there is a very considerable commercial interest in providing especially the continuously (float or otherwise) produced types of sheet glass, all of which are almost without exception of the float glass type, with an electrically conducting, IR reflecting layer. According to currently available technology, an unclouded layer is obtained only if the sheet of glass, prior to being heated to approximately 600°C, is dipped into a methyl ester silicate solution and withdrawn therefrom at an even rate.

An SiO<sub>2</sub> layer which provides a barrier against alkali is formed after heating. For the same purpose, it has also been proposed to apply oxide layers of silver, aluminum, antimony copper, iron, cobalt, nickel, thallium and zinc (U.S. Patent No. 2,617,741). However, as applied to the treatment of individual sheets of glass, this method has the distinct drawback of requiring a preliminary dipping process followed by the spraying operation. This is totally unsuitable for the commercially highly desirable continuous treatment of material.

As regards the latter kind of treatment, it is possible to coat float glass directly, i.e. without a barrier layer, with chlorine-free dibutyl tin diacetate or similar compounds. This will produce unclouded layers which are however of little commercial interest owing to their poor conductivity. If one attempts to improve conductivity by HF doping, there is inevitably a precipitation of imperfectly soluble alkyl-tin-fluorides in the solution. The poor solubility of this type of compound is well known and this class or type of compound which has very low solubility will always be formed when organic stannic compounds are in the presence of the fluoride ion F<sup>-</sup>. Whilst British Patent specification 965,792, in

table 1, lists certain "solutions" which, as for example in Nos. 6 to 8, contain dibutyl tin oxide, ammonium acetate, hydrofluoric acid in alcohol, n-propanol and little hydrochloric acid, reproduction tests have shown that these are in fact suspensions and not solutions.

Among the expensive C—F compounds which do not produce this undesirable reaction, trifluoroacetic acid is still the cheapest. According to the prior art, an F<sup>-</sup> doping treatment which is after all applied at about 600°C may also be carried out with trifluoroacetic acid. Whilst unclouded layers with good conductivity are obtained in this way, the price of the organic tin compound is about double that of SnCl<sub>4</sub>, and trifluoroacetic acid costs about ten times as much as HF. Since in every spraying process only a very small part of the sprayed substance is converted into a coating layer, the price of the spraying solution is a very important consideration.

A certain measure of progress, eliminating trifluoroacetic acid and its high costs but retaining dibutyl stannic oxide which, after all, costs still twice as much as SnCl<sub>4</sub>, is shown in German OS 2806468 according to which the organic tin compound (only dibutyl tin oxide is actually disclosed) is sprayed on in powder form. The F<sup>-</sup> doping which is necessary for achieving satisfactory conductivity can be obtained by cheap HF, especially if this is admixed only immediately prior to entering the spraying nozzle.

For achieving the most economical coating method therefore especially with regard to float glass the application of an SnCl<sub>4</sub> solution can be the only one under consideration. This, in turn, necessitates, in the case of alkali-rich glass, the provision—by spraying because with continuous material no other method is possible—of a barrier layer of the kind obtained by dipping as hereinbefore described.

For this purpose, U.S. Patent No. 2,617,741 suggests the earlier mentioned oxides of Ag, Al, Sb, Cu, Fe, Co, Ni, Tl and Zn, whilst pointing out at the same time under column 2, lines 38—45 and in other places that at temperatures in excess of 400°F and after any time longer than one minute, alkali may migrate through the barrier layer to the surface where the Na Cl reaction which causes the clouding may still take place. Whilst the expedient suggested there of spraying with an aqueous solution for barrier layer formation will, owing to the high evaporation heat of the water, quickly reduce the temperature of the substrate to a non-critical value for sodium migration after the barrier layer has been formed, it is necessary to re-heat for SnO<sub>2</sub> coating to temperatures which are most certainly critical, as is evident from the quoted conductivity of no more than 125Ω/□.

Furthermore, such reheating is highly uneconomical from the point of view of time and energy consumption. The above mentioned U.S. Patent also specifies that both sides of a glass sheet material should be coated with a barrier layer in order to avoid distortion during the application of the conducting layer. This again is

expensive and cannot be done in a float process.

The present invention therefore sets out to develop a method which has none of the disadvantages of the prior art, which works "on line" and as well as for coating cut lengths of sheet glass is suitable for use in a continuous (endless) process, requiring only a single heating up of the individual sheets of glass or managing to work with the available amount of heat in a continuously produced endless material, and which essentially requires the cheapest possible spraying solution of  $\text{SnCl}_4$  and HF to build up the conductive layers, whilst only for a very brief preliminary spraying period a thick alkali barrier layer is built up by means of a dibutyl tin oxide solution.

The method is characterised in that an alkali-rich glass, heated to approximately  $630^\circ\text{C}$ , is briefly sprayed with a solution of a dialkyl tin oxide—for reasons of economy dibutyltin oxide is preferred—for only a sufficient length of time to form a very thin alkali-barrier layer of  $\text{SnO}_2$  and that immediately afterwards and without reheating, spraying is continued from a second nozzle with a *per se* known HF-doped  $\text{SnCl}_4$  solution until an unclouded  $\text{SnO}_2$  layer with  $20\text{—}30\Omega/\square$  is formed.

In order to solve the stated problem in the manner proposed by the present invention, it was necessary to surmount a number of existing prejudices. As far as the thin  $\text{SnO}_2$ -alkali barrier layer is concerned, it was reasonable to expect that, at the high temperatures of  $>600^\circ\text{C}$ , the alkali would migrate into the  $\text{SnO}_2$  stratum and react with the following  $\text{SnCl}_4$ , as described in the above cited prior art. It is also a well known fact that alkali migration "poisons" the conductivity of the  $\text{SnO}_2$  layer. Surprisingly however, the conductivity was found to be equally good as on low alkali glass and there is no clouding effect. There were no known indications that  $\text{SnO}_2$  might behave so completely differently from the numerous oxides of other metals listed previously. This applies especially for such thin layers as result from an extremely brief spray application which will not cause a significant drop in the temperature of the glass sheet so that coating may continue without re-heating. Another advantage is seen to reside in that a uniform  $\text{SnO}_2$  layer is produced despite the fact that two spraying solutions are applied. According to the prior art, there are always stratifications of barrier layer and conducting layer with all the chemical and optical boundary and interface-problems associated therewith.

Whilst the  $\text{SnO}_2$  layers obtained in accordance with this invention are unclouded, they nevertheless have a distinct iridescence or opalescence arising from minor variations in layer thickness in the region of interference layer thickness. This may be very largely suppressed by making the alkali barrier layer of the dialkyltin oxide solution somewhat thicker than necessary simply by extending the coating time.

Immediately afterwards spraying continues with

the HF-doped  $\text{SnCl}_4$  solution. The resulting thicker strata are distinctly more homogeneous in colour.

The invention is more specifically explained in the following examples wherein the mutually interdependent concentrations and spraying times may vary within wide limits. The appropriate combination for a given application can be easily determined by a few manual tests.

#### Example 1

A float glass sheet at  $630^\circ\text{C}$  is first sprayed by means of a spraying nozzle for three seconds with:

##### solution A:

120 g DBTO (dibutyltin oxide)

200 ml acetone

400 ml methanol

30 ml acetic acid (98% by weight)

This forms a low conductivity, thin  $\text{SnO}_2$  layer on which spraying is directly and without reheating continued for 8 seconds with:

##### solution B:

200 ml  $\text{SnCl}_4$

780 ml methanol

20 ml HF (40%)

This produces a clear unclouded layer with  $R=20\Omega/\square$ .

R values between  $R=20\text{—}1000\Omega/\square$  are obtained by varying the concentrations in solution B and the spraying time.

#### 95 Example 2

A float glass sheet at  $630^\circ\text{C}$  is coated with solution A as in Example 1, but the spraying time is trebled to 9 seconds so that a thick  $\text{SnO}_2$  layer with little conductivity is formed. On top of this layer, coating is continued with solution B as in Example 1. A clear, unclouded layer is formed with  $R=20\Omega/\square$ , which however, thanks to the thick substratum (under or barrier layer) is taken out of the interference range and more homogeneous in colour than the result obtained in Example 1 wherein minor variations in layer thickness become very apparent because of the formation of interference colours.

#### Claims

1. A method of producing an unclouded electrically conductive  $\text{SnO}_2$  layer on alkali-rich glass comprising the steps of spraying a solution of a dialkyl tin oxide in an organic solvent onto a surface of the glass heated to about  $600^\circ\text{C}$ ; and then, immediately and without reheating the glass, spraying a solution of tin tetrachloride and hydrofluoric acid in an organic solvent onto the  $\text{SnO}_2$  layer formed as a result of the first spraying step.

2. A method as claimed in Claim 1 wherein the dialkyl tin oxide is dibutyl tin oxide.

3. A method as claimed in Claim 1 or 2, wherein the first-mentioned spraying step is effected for a short time to produce a first  $\text{SnO}_2$  layer which is thin.

4. A method as claimed in Claim 1 or 2,

wherein the first-mentioned spraying operation is effected for a relatively long time to produce a first SnO<sub>2</sub> layer which is thick.

5 A method of producing an unclouded electrically conductive SnO<sub>2</sub> layer on an alkali-rich glass substantially as hereinbefore described in

Example 1 or Example 2.

10 6. An alkali-rich glass having an unclouded electrically conductive SnO<sub>2</sub> layer thereon, when produced by the method as claimed in any preceding claim.