PROCESS FOR REMOVING THIN FILMS OF COBALT OXIDE FROM VITREOUS SURFACES

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The present invention relates broadly to films of metal compounds and more particularly to the removal of such films from surfaces to which they have been applied.

This application is a continuation-in-part of my copending application Serial No. 841,724, now abandoned, filed September 23, 1959.

Ultra-thin, transparent films of metal compounds, particularly the oxides and to some extent the fluorides, have recently come into rather wide use for a number of purposes ranging from electrical conductivity to light modification.

By way of example only, it may be mentioned that certain light modifying films have recently found an important place in the automotive industry. This arose from the fact that in the present-day large rear windows or backlights for automobiles, passengers experience considerable discomfort from the sun's rays through the unusual expanse of glass which extends well into the roof of the car.

In order to overcome this problem it has been proposed to apply a film, such as a very thin cobalt oxide film, along the upper area of the rear window to reduce the transmission of objectionable components of the sun's rays while at the same time preserving a substantial amount of visibility through the window.

However, there are instances where it is found upon critical inspection, after it has been applied, that the film is not sufficiently perfect for commercial acceptance. In this event, removal of the film is desirable so that the expensive bent, polished plate glass window need not be scrapped but may be reprocessed to produce a new backlight with a satisfactory film. There are also instances where it is necessary or desirable to delete portions of thin films from selected areas only of a filmed or partially filmed base or to remove part of a film in order to reduce its thickness.

Accordingly, the primary object of this invention is to provide a novel and improved way in which part or all of an ultra-thin film can be removed from its supporting base.

A more specific object is the provision of a method of removing metal compound films from vitreous surfaces.

A still more specific object is to provide a procedure for removing thin, transparent cobalt oxide films from glass surfaces.

Further objects and advantages of the invention will become more apparent during the course of the following description when taken in connection with the accompanying drawings.

In the drawings, wherein like numerals are employed to designate like parts throughout the same:

The single figure is a graphic comparison of the removal times and temperatures for removal agents of different compositions.

Broadly speaking, the process of the present invention is effected by subjecting a surface, filmed with a metal compound, to a heated aqueous solution of phosphoric acid containing a small percentage of a film solution accelerator, namely a ferrous ion. The ferrous ion may be supplied by means of a suitable ferrous compound of appropriate solubility and it has been found that ferrous sulfate and ferrous chloride are satisfactory for this purpose.

The concentration of phosphoric acid may be in the range from 50 weight percent to 85 weight percent; and, it has been found desirable to practice the invention at an acid concentration of about 80 to 85 percent. Any grade of phosphoric acid of the desired concentration may be employed. However, we have preferred to use technical grade phosphoric acid which contains 85% acid and has a specific gravity of 1.689 (11.98 pounds per gallon).

The ferrous ion may be employed in a range from about 0.25% to about 5.0% based on the weight of the phosphoric acid. The upper limit of ferrous ion is determined by the solubility in phosphoric acid of the ferrous compound employed to furnish the ferrous ion. For example, at 266° F., ferrous sulfate is soluble in 85% phosphoric acid to the extent of 1.6% iron; ferrous chloride is soluble to the extent of 4.6% iron at this temperature.

It is to be understood that, while the present invention is in no way limited to use with films of any specific metal compound or to the removal of films from any specific supporting surface, it has been found to be particularly effective in removing cobalt oxide films from glass and, for purposes of illustration, will be specifically described in that connection here.

The deletion rates of compositions of the present invention are all temperature dependent. In FIG. 1, curve A, the time in seconds to remove a 30% transmitting film of cobalt oxide is plotted against the acid temperature; a 30% transmitting film of cobalt oxide transferred from Illuminant C (artificial daylight). It will be seen that at a temperature of 140° F., approximately 100 seconds are required for a solution containing 85% phosphoric acid and 1% ferrous sulfate to remove the film. On the other hand, at a temperature of 350° F., the deletion time is reduced to approximately 2 seconds. Thus temperatures in the range from 140° F. to 350° F. are within the scope of the present invention. However, for preferred operation, the process is practiced at a temperature in the range from about 212° F. to about 250° F. By so operating, the acid concentration of the treating bath will be retained substantially constant because the water loss therefrom due to evaporation will be approximately negligible.

The film removing composition is suitably made by adding the ferrous compound as a concentrated aqueous solution to the aqueous phosphoric acid. The water in which the ferrous compound is dissolved will evaporate when the acid solution is heated to an operating temperature of about 250° F.

Where the ferrous compound is ferrous sulfate, the addition of solid ferrous sulfate to the phosphoric acid to form the film removing solution is to be avoided since ferrous sulfate is only slowly soluble in phosphoric acid. Also a 1% concentration of ferrous sulfate is recommended as a working figure because of the possibility that higher concentrations may recrystallize on cooling.

Where the ferrous compound is ferrous chloride, however, the addition of solid ferrous chloride to the phosphoric acid to form the film removing solution is practicable due to the higher solubility in the phosphoric acid. Higher concentrations of ferrous chloride, depending upon acid concentration and temperature, can also be employed in contrast to the ferrous sulfate due to the higher solubility of the ferrous chloride.

Ferrous sulfate is soluble in water at room temperature (70° F.) to the extent of 1.2 pounds per gallon. The aqueous ferrous sulfate addition solution can therefore be made up to this concentration. Thus, one gallon of the ad-
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3. A dilution agent may be employed for every 10 gallons or 120 pounds of 85% phosphoric acid to make a working solution containing 1% by weight of ferrous sulfate. This will provide approximately 0.3% ferrous ion in the solution.

As an example, ferrous chloride (FeCl₂·4H₂O) is soluble in water at 50° F. to the extent of approximately 14 pounds per gallon. The aqueous ferrous chloride addition solution can therefore be made up to this concentration. Thus one gallon of the addition agent may be employed for every 23.3 gallons or 280 pounds of 85% phosphoric acid to make a working solution containing about 5% by weight of ferrous chloride. This will provide approximately 1.5% of ferrous ion in the solution.

The ferrous ion is slowly exhausted as filmed glass is treated in the bath. However, the ferrous ion concentration can be maintained substantially constant by adding a suitable amount of the ferrous compound to the phosphoric acid make-up which is required to replace that removed by the deleted flocks.

The curve A shown in FIG. 1 represents the times required for completely deleting a 30% transmitting cobalt oxide film. However, many automobile back windows are rejected because of spots, which are heavy deposits of cobalt oxide. These spots usually require 2 to 3 times the deleting time of the film.

The novelty of the present invention is highlighted by the following example:

Example 1

Removal rates of FIG. 1 were plotted by making a series of runs wherein a bath of aqueous phosphoric acid of a concentration of 85 weight percent acid, and containing 1% by weight of ferrous sulfate, was heated at increasing temperature increments in the range from about 140° F. to about 350° F.

At each temperature level a sheet of glass, containing a 30% transmitting cobalt oxide film was immersed in the bath for the time required for film removal. Thereafter the glass was removed, rinsed and dried. Removal times were plotted against temperature as curve A.

Runs were also made wherein the bath consisted of aqueous phosphoric acid of a concentration of 85 weight percent, with no ferrous sulfate added. Removal times were plotted against temperatures as curve B.

It will be seen from FIG. 1 that the removal rates plotted by curve A are unexpectedly higher than those of phosphoric acid alone in curve B.

Thus curve A shows that the combination of phosphoric acid and ferrous sulfate is about 30 times faster than phosphoric acid at the same temperature.

The invention is applicable to the treatment of both tempered and untempered glass. Generally the thermal shock encountered when treating tempered glass of room temperature will be harmless. However, when treating untempered glass, it may be necessary to heat the glass to about the temperature of the acid bath before immersion to avoid breakage.

The invention is applicable to the removal of films from vitreous surfaces in general, including glass, quartz, porcelain and the like.

While the invention has been specifically described in its preferred embodiment as immersing a glass sheet either cold or heated, to a film-removing bath, it is to be included within the scope of the invention to heat the glass sheet to a suitable deliming temperature and apply the film-removing solution to the sheet by spraying, brushing or the like.

It will be understood that this invention is susceptible to modification in order to adapt it to different uses and conditions and accordingly, it is desired to comprehend such modifications within the scope of the appended claims.

I claim:

1. A process for removing a film of cobalt oxide from a vitreous surface, the steps of subjecting the filmed surface to the action of an aqueous solution of phosphoric acid, in a concentration in the range of about 50 to 85% by weight, with a ferrous ion, in a range from about 0.25% to 3.0% based on the weight of the phosphoric acid, at a temperature in the range from about 140° F. to about 350° F.

2. A process as defined in claim 1 wherein the solution is at a temperature in the range from about 212° F. to about 350° F.

3. A process for removing a film of cobalt oxide from a vitreous surface including the steps of, providing a bath made up of an aqueous solution of phosphoric acid of a concentration in the range from about 50 to about 85% by weight and ferrous ion equal to at least 0.5% by weight of the phosphoric acid, said ferrous ion being supplied by adding ferrous sulfate to said acid, heating said bath to a temperature in the range from about 140° F. to about 350° F., subjecting said filmed surface to said bath for a time sufficient to remove the film, and removing the solution from the vitreous surface.

4. A process as defined in claim 3 wherein the bath is heated to a temperature in the range from about 212° F. to about 350° F.

5. A process for removing a film of cobalt oxide from a vitreous surface including the steps of, providing a bath made up of an aqueous solution of phosphoric acid of a concentration in the range from about 50 to about 85% by weight and ferrous ion equal to at least 0.5% by weight of the phosphoric acid, said ferrous ion being supplied by adding ferrous sulfate to said acid, heating said bath to a temperature in the range from about 140° F. to about 350° F., subjecting said filmed surface to said bath for a time sufficient to remove the film, and removing the solution from the vitreous surface.

6. A process as defined in claim 5 wherein the bath is heated to a temperature in the range from about 212° F. to about 350° F.

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