Patented May 5, 1953

2,637,670

UNITED STATES PATENT OFFICE

2,637,670

PROCESS FOR THE STRIPPING OF MIRROR BACKING

Keith E. Brown, San Gabriel, and Francis E. Clark and Clark E. Jackson, Alhambra, Calif., assignors to Turco Products, Inc., Los Angeles, Calif., a corporation of California

No Drawing. Application January 17, 1947, Serial No. 722,768

11 Claims. (Cl. 134—29)

1

This invention relates to processes for the removal of silver from mirrors. In order that our invention may be better understood, it may be useful to consider the methods now employed commercially in forming mirrors and in removing silver films from mirrors.

Processes now employed commercially in the manufacture of mirrors do not differ substantially from that originally introduced by Baron Liebig about one hundred years ago. Liebig discovered that an ammoniacal silver nitrate solution will deposit silver in the presence of a reducing agent upon a heated glass surface. The mixed ingredients are poured out on a glass to be silvered and the silver is deposited from the mixture. It is then washed and cleaned. Except for relatively minor changes in the composition of the reducing solutions, the present silvering solutions are essentially the same as used by Liebig. Two main classifications of such processes are now employed: one in which the temperature is held at about atmospheric, and the other, the hot process, wherein the temperature is elevated. The solutions employed are somewhat different.

It is also usual to coat the silvered surface with shellac and paint or other organic coating compositions. Such coatings are frequently filled with metallic powder such as aluminum, bronze, or copper powder and sometimes filled with fillers such as calcium carbonate.

The usual practice heretofore employed in removing such silver from the glass in order to reclaim the glass and the silver involves a removal of the organic coating by caustic alkali and the subsequent corrosion, i. e., solution, of the silver by means of corrosive acids such as sulphuric, nitric or hydrochloric. The conventional commercial method heretofore employed is illustrated by the following procedure:

The silver backing of the mirror is scrubbed with caustic soda and allowed to stand from 45 minutes to an hour in contact with caustic soda. This usually loosens the paint and shellac which are rinsed off with a garden hose. Hydrochloric acid mixed with nitric acid is then applied and the silver is scrubbed with a brush. This usually takes from about 15 to 20 minutes. The excess acid is washed off and any remaining silver is cleaned off with ammonia. Instead of muriatic acid, sulphuric acid or nitric acid may be employed. All such acids act to corrode or eat away the silver by solution thereof or conversion into a salt. Not only is this process slow, costly and results in the formation of impure dilute

2

solutions and suspension of silver salts which are difficult to reclaim, but also the corrosive nature of the acids requires the use of wooden tanks since steel tanks corrode. Wooden tanks deteriorate rapidly in this service. The process is also a health hazard since the mirrors must be scrubbed with caustic alkali and then with acid.

We have found that we can remove the silver from a silvered mirror without material corrosion or solution of the silver. The silver is removed as metallic silver in relatively large strips or sheets. We may thus speed up to a great extent the process of the removal of such silver and recover the silver as silver, i. e., without destroying the metallic nature thereof. Instead of corroding the silver we destroy the bond between the metallic silver film and the glass and thus permit the metallic film to be removed from the glass surface without material destruction of the nature of the silver forming the film.

We have found that a solution of a soluble inorganic sulfide, such as alkali metal sulfide, or ammonium sulfide is active to remove silver films from glass mirrors without any material destruction or corrosion; that is, solution of the silver metal. While some superficial blackening of the metal occurs, this is apparently merely a film formation, the metal coming off in the main as metal in large sheets or strips.

The sulfide acts apparently to destroy the bond between the metal film and the glass and to cause separation therefrom. When the mirror is coated with shellac or paint the alkaline nature of the stripping agent destroys the integrity of the organic coating, causing it to soften and swell and to slough off, permitting the agent to attack the bond between the silver mirror and the glass to cause the separation of the silver mirror film. If desired, paint or shellac removing solvent or softener may be used, and where the coating is of the synthetic resin type, a solvent which dissolves or softens such coatings may be employed.

The softening agent or solvent for the paint or other organic coating may be miscible or non-miscible with water solution of the reagent. Either of them is useful in destroying the integrity of the mirror backing or coating.

It is therefore possible to use any of the conventional paint removing solvents and the shellac removing solvents which have been employed heretofore in the paint and shellac removing art and the identification or selection of the particular organic solvents to be employed in our com-

position will depend upon the specific nature of the organic coating employed with the mirror. Thus, where the coating is of a synthetic resin type or synthetic resin lacquer, one may select any of the solvents listed by Simonds and Ellis in their Handbook of Plastics, published by Van Nostrund Co., 7th printing, pages 240 to 249, and select the particular solvent by reference to the solubility therein of the particular resin type employed in organic coatings, and said list is hereby incorporated by reference.

Where the coating is of the shellac type or oil paint type, a suitable alcohol or glycol or glycol ether or ether may be employed. For example, we may employ monohydric and polyhydric alcohol, such as methyl, ethyl, propyl, or isopropyl alcohol, and employ also the polyhydric alcohols, such as glycol or glycerine and the ethers of such glycols, for example, ethylene glycol, propylene glycol, diethylene glycol, hexane 1, 2 diol, diethylene glycol, polyethylene glycol, glycerine, the glycol ethers, such as ethylene glycol monoethyl ether, butyl ether, ethylene glycol monopropyl ether. We may employ the ketones, such as acetone, methyl ethyl ketone, diethyl ketone, acetonyl acetone, isophorone, diacetone alcohol. We may employ the chlorinated compounds, such as methylene chloride, ethylene chloride, trichlorethylene, dichlorethylene, monochlor benzene and dichlor benzene. All of these are listed merely to illustrate the nature of the solvents employed and are not intended to limit the scope of the invention to such listed compounds. All of such compounds have solvent action for the protective films as described above.

It has been found desirable to choose from the above solvents, when the process is to be carried out at an elevated temperature, those solvents whose flash point is sufficiently high to be safe at the elevated temperature employed. Thus, when the solvent is miscible with water the flash point (determined by the Cleveland open cup method) should be 150° F., and if not miscible with water, 200° F., when using these materials in the process at temperatures specified below as suitable, i. e., 160° to 190° F.

The organic solvent need not be miscible with water provided the materials are kept agitated in use. In selecting the solvent the solubility of the coating in the solvent is the criterion, as will be understood by those skilled in this art. Additionally, the solvent should have a boiling point sufficiently high to avoid danger of excessive evaporation fire. Thus, for example, where a temperature of 175° F. is used in the process, as is more fully set forth below, the flash point of the solvent if soluble in water should be above about 200° F. and if not miscible with water it should be above about 150° F. If the process is carried out at room temperature the boiling point of the solvent should be preferably above the temperature of the treatment if it is not miscible with water, and if miscible with water its partial pressure in the solvent should be adjusted by selecting solvent of proper boiling point or by adjusting the concentration or both so that excessive evaporation is avoided. A material with a boiling point at or near room temperature, i. e., above about 50° to 60° F. will be sufficient to meet this requirement.

In addition to or instead of the solvent we way also employ the alkali metal sulfide in alkaline solution, employing preferably an alkaline metal hydroxide or ammonium hydroxide.

The process may be carried out by immersing the mirrors in a solution of the sulfide and allowing them to remain for a time sufficient to strip the mirrors at temperatures ranging from atmospheric, i. e., 40 to 60° F., or at an elevated temperature up to about 200° F. After the mirrors have been left in the solution for a sufficient time the mirror backing is loosened and strips off and the mirror may then be rinsed with water to remove any of the solution or mechanically adhering strips off the mirror.

We have found that the activity of the sulfide ion in removing the mirror backing is materially improved by the presence of the ammonium ion. Thus, if to the alkali metal sulfide, i. e., sulfide of sodium, potassium, lithium or strontium or ammonia, we add ammonium hydroxide or ammonium carbonate, or if ammonium sulfide is employed the stripping activity is improved. Instead of using the sulfide we may use the polysulfides or the hydrosulfide of the alkali metal or of ammonia. The term "alkali metal sulfide" as used herein is intended to include the polysulfide and hydrosulfide of the metal. The term "alkali metal" as used herein is intended to include ammonium.

The higher the temperature the more rapid the stripping action. The temperature, however, should not be at boiling or too high in order to avoid loss of solvent, if any is used, and to avoid excessive evaporation of water.

The activity of these sulfides in removing the backing is exemplified by the following examples as given by way of illustration and not as a limitation:

Example 1

10 parts by weight solution of sodium hydroxide and 5 parts by weight of sodium sulfide (Na_2S) are dissolved in 85 parts by weight of distilled water. Mirrors immersed at temperatures of about 175° F. were completely stripped of the silver in about 45 minutes.

Example 2

A solution composed of 5% by weight of sodium sulfide (Na_2S); 10% by weight of ammonium carbonate; 85% by weight of distilled water was employed in the place of the solution of Example 1 on another portion of the same mirror. The mirror was treated as in Example 1 by immersion of the mirror in the solution at 175° F. The mirror was stripped in about 1 minute.

In both of these examples the mirror was not coated with either shellac or paint but merely had a silver film deposited on the glass in order that the activity of the ammonium ion and the sulfide ion be more clearly revealed.

Sodium sulfide is also effective in the removal of silver mirrors which are backed with an organic coating composition such as shellac or paint, as is common in the mirror forming art. This is exemplified by the following:

Example 3

A solution composed of .5 part by weight of a wetting agent, sodium salt of an alkyl aryl sulfonic acid; 90 parts by weight of a 10% solution of KOH; 54 parts by weight of $Na_2S{-}9H_2O$; 315 parts by weight of distilled water, adding up to a total of 459.5 parts by weight of reagent, was formulated, and the mirror immersed in the solution at a temperature of 23° C. The mirror was stripped completely in from 10 to 20 minutes.

This material is effective and its effectiveness may also be improved by the addition of one of the solvents as for the paint backing as previously

described. For example, the addition of about 10 parts by weight of cresol is useful in aiding the removal of the paint and shellac backing.

The activity of this material is also aided by the use of an ammonium ion in the mixture. Part or all of the KOH may be replaced by K_2CO_3, NaOH, Na_2CO_3, LiOH, Li_2CO_3; $Sr(OH)_2$; $SrCO_3$; NH_4OH or $(NH_4)_2CO_3$.

The concentration of the sulfide and alkali which may be employed will vary with the nature of the coating and depend on the presence of auxiliary organic coating softeners or removers or solvents. The solutions should be of concentrations such that they are not too viscous. Concentrations of sulfide, ranging from about 1 to about 25% by weight, and alkali in about the same range will be found suitable. The solvent may be added in the desired proportions to soften the film, said proportions ranging from 0 to 50%.

Usually where defective mirrors from a mirror production line are to be processed so that all the mirrors are similarly formed, it will be desirable to test a sample of the mirrors by the procedures set forth in Examples 1 to 3 and adjust the proportions of the ingredients to give the best results.

While we have described a particular embodiment of our invention for the purpose of illustration, it should be understood that various modifications and adaptations thereof may be made within the spirit of the invention as set forth in the appended claims.

We claim:

1. A process of removing silver mirror films from glass which comprises immersing said mirror in a mirror stripping agent comprising a water solution of an alkali metal sulfide, said solution containing ammonium ions at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

2. A process of removing silver mirror films from glass which comprises immersing said mirror in a mirror stripping agent comprising an alkaline water solution of an alkali metal sulfide, said solution also containing ammonium ions at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

3. A process of removing silver mirror films from glass which comprises immersing said mirror in a mirror stripping agent comprising an alkaline water solution of sodium sulfide and a soluble ammonium compound and an organic paint removing solvent at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

4. A process of removing silver mirror films from glass which comprises immersing said mirror in a mirror stripping agent comprising a water solution of sodium sulfide and ammonium carbonate at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

5. A process of removing silver mirror films from glass which comprises immersing said mirror in a mirror stripping agent comprising a water solution containing from 1 to 25% of an alkali metal sulfide and from 1 to 25% of an alkali and from 0 to 50% of an organic paint removing solvent at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

6. A process for removing silver mirror films from glass, which comprises immersing the mirror in a mirror stripping agent comprising a water solution containing sulfide ions and ammonium ions at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

7. A process for removing silver mirror films from glass carrying an organic coating, which comprises immersing the mirror in a mirror stripping agent comprising a mixture of a water solution containing sulfide and ammonium ions and a paint removing solvent at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

8. A process for removing silver mirror films from glass, which comprises immersing the mirror in a mirror stripping agent comprising a water solution containing sulfide ions at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

9. A process for removing silver mirror films from glass carrying an organic coating, which comprises immersing the mirror in a mirror stripping agent comprising a mixture of a water solution containing sulfide ions and a paint removing solvent at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

10. A process for removing silver mirror films from glass, which comprises immersing the mirror in a mirror stripping agent comprising an alkaline water solution containing sulfide ions at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

11. A process for removing silver mirror films from glass carrying an organic coating, which comprises immersing the mirror in a mirror stripping agent comprising a mixture of an alkaline water solution containing sulfide ions and a paint removing solvent at a temperature in the range of atmospheric to about 175° F., removing the mirror film from the glass, and washing the glass.

KEITH E. BROWN.
FRANCIS E. CLARK.
CLARK E. JACKSON.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
242,338	Laval	May 31, 1881
1,495,547	Clark	May 27, 1924
2,215,507	Hunlock	Sept. 24, 1940

OTHER REFERENCES

Chemical Formulary, Bennett, vol. 4 (1939), pages 64, 154 and 155. (Copy in Scientific Library.)

Chemical Formulary, Bennett, Chem. Pub. Co., N. Y., vol. 6 (1943), page 222. (Copy in Scientific Library.)