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PROCESS FOR THE STRIPPING OF MIRROR BACKING

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This invention relates to processes for the removal of silver from mirrors and to compositions of matter useful in such processes. 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 mixed with nitric acid. 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 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. 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 and costly and results in the formation

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of impure dilute 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 dilute solution of an alkali metal halide or ammonium halide, when applied to the backing of a silver film of a mirror, will separate the silver film from the glass surface. The silver film is removed in relatively large sheets or pieces from the glass surface as metallic silver without any substantial corrosion, solution, or other destruction of the metallic nature of the silver film.

These salts are active apparently in separating the bond between the silver film and the glass surface. The relative activity of the various halogen salts of these monovalent alkali metals and ammonium ions depends on the nature of the halide ion. We have found that the activity of the halide salts when measured as the time necessary to strip silver film from a glass mirror decreases from iodide to bromide to chloride to fluoride. The time necessary to strip such a mirror increases in the above stated order. The activity of the bromide salts is so great that it is apparently not materially affected by pH, and thus the activity of the iodide salts is about in the same order of magnitude irrespective of whether the pH value is one or less or eleven.

Where the silvered mirror is backed with an organic coating composition, it is desirable to incorporate in the stripping reagent some material which will attack the integrity of the organic coat and soften it or remove the coat. We have found that it is not necessary that the organic coating be dissolved, since any agent which will cause a destruction of the integrity of the coat

is sufficient. Presumably it is sufficient to soften or loosen the coat to permit the penetration of the mirror stripping agent. We have found that either organic paint removing solvents or alkaline materials are suitable for this purpose. Wetting agents may be added although this is not essential. Suitable wetting agents are those listed in the Journal of Industrial Engineering Chemistry, vol. 35, pp. 126–130, January 1943.

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 composition 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 Nostrand 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. It is to be noted, however, that where the solvent is to be employed in an acid solution of phosphoric acid, solvents which react with the phosphoric acid, such as amines, especially water soluble amines, should be avoided.

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 process is carried out by immersing the mirror in the solution of the stripping agent at temperatures ranging from ordinary atmospheric room temperature up to boiling. The higher the temperature the more active the reaction for any particular material. It is desirable especially when using a volatile solvent to hold the temperature below the boiling point of the solution or solvent in order to avoid evaporation loss and hazards. We have found that temperatures ranging from about 70° to 200° F. are suitable depending upon the nature of the solvent. Lower temperatures may be employed where the solvent reagent is more active and higher temperatures are suitable for the less active reagent, as will appear from the exemplifications hereinafter set forth.

The solution of halogen salts with or without wetting agents and with or without the organic paint removing solvent or with or without the acid or alkali are substantially non-corrosive either to the silver of the mirror or to steel, especially stainless steel, and therefore the process may be carried out in stainless steel tanks at relatively high temperatures if desired. The removal of the film is by means of physico-chemical process rather than by corrosion action or mechanical attrition as in the prior art.

It has been found that the immersion of the mirror in the solution without mechanical attrition causes a separation of both the organic coating and the silver film from the glass, depending upon the nature of the halogen salt and the nature of the coating and the temperature employed, in times much shorter than those required by any of the prior art processes. After immersion for a proper length of time the mirror is removed from the solution and rinsed. Any adhering silver is removed by employing a spray of water.

EXAMPLE 1

The organic coating is omitted in the process of Example 1 in order that the effect of the organic coating does not obscure the activity of the halogen.

Solutions A to T were made up according to the following formulations given in the table:

Table

Sol.	COMPOSITION		
	Salt	Percent by weight of Salt	Adjusted pH
A	KI	9	1
B	KI	9	3
C	KI	9	6
D	KI	9	8
E	KI	9	11
F	NaBr	8	1
G	NaBr	8	3
H	NaBr	8	6
I	NaBr	8	8
J	NaBr	8	11
K	NaCl	8	1
L	NaCl	8	3
M	NaCl	8	6
N	NaCl	8	8
O	NaCl	8	11
P	NaF	8	1
Q	NaF	8	4
R	NaF	8	7
S	NaF	8	9
T	NaF	8	11

Each solution was adjusted to the pH as given in the table by titrating the solution with a dilute nitrate or caustic soda or mixtures thereof. Thus the potassium iodide was a 9% solution in distilled water titrated with nitric acid and sodium hydroxide to adjust the pH to the values given. The sodium salts were all 8% solutions in distilled water titrated with nitric acid and sodium hydroxide to the pH as given.

It was found that the potassium iodide solution irrespective of the pH stripped the silver from the mirror in less than 15 minutes. No significant difference between the various solutions A to E with respect to the rate of stripping was observed. Apparently the iodide ion is so active that it will strip the mirror both in highly acid and highly alkaline as well as neutral solutions.

In the case of the sodium bromide, it was found that these solutions as well as the other halide solutions were much slower acting than the iodide solution. No significant difference could be found between the activity of any halogen salt of the various alkali metals or ammonium.

In the case of the bromides, fluorides and chlorides, however, the activity increases as the pH decreases. Solution F stripped the mirrors under 10 minutes, and solutions G and H required from 10 to 20 minutes, while the solutions I and J required from 20 to 30 minutes. The chloride seemed to be less active than the bromide at like pH values, and the fluoride appears least active at the same pH values. Solution K stripped the mirror formed by the hot process in 15 minutes; solutions L stripped such mirror in about 30 minutes; solutions M stripped such mirror in about 40 to 45 minutes; solutions N required about an hour; solutions O required about 48 hours to strip such mirror.

While the iodide and the bromide have similar activities in the stripping of mirrors when formed by either the hot or cold process, in the case of the chloride the stripping rate is different in the case of mirrors formed by the hot process from those formed by the cold process. In the case of mirrors formed by the hot process, the activity of the sodium chloride at pH's of 1 or 3 on either of the silver mirrors is substantially the same. No substantial difference is the activity appears in the case of the sodium chloride solution at pH of 11 on the silver mirrors formed by either process. In the case of the mirror formed by the cold process a longer time was required than that given above for the hot process silver mirrors when employing the NaCl solutions at pH of 6 or 8. It required more than 48 hours to strip a mirror formed by the hot process.

A similar experience was had with the fluoride salts. Solution P removed the silver mirror formed by either the hot or cold process from the glass in less than 30 minutes. The solutions Q and T removed the mirror backing in 48 hours, while the solutions R and S required 48 hours.

All of the processes thus exemplified were carried out at a temperature of 175° F.

In employing our silver mirror stripping agent with mirrors which are also coated with organic coating composition, it is desirable to employ with such stripping agent a component which will act to soften or dissolve or otherwise destroy the organic coating. Such agent is one of the organic coating softening agents previously referred to, or in place thereof or in addition thereto the halide stripping agent may be employed in an alkaline solution. In employing the organic coating softening agent such as the solvents previously referred to we may also employ the halide stripping agent in acid solution. This is exemplified by the composition and process of Example 2:

EXAMPLE 2

The stripping agent was made up according to the following formulation:

27 parts distilled water; 3 parts sodium chloride; 50 parts of a 75% solution of orthophosphoric acid; 20 parts of an organic softening agent composed of 18 parts of acetone; and 2 parts of ethylene glycol.

The solution as formulated above was mixed with equal parts of distilled water and a mirror coated with an organic coating composition, in this case shellac and paint, was immersed at the temperature of 80° F. and then rinsed. The mirror was completely stripped in from 10 to 15 minutes.

This solution is substantially non-corrosive to a steel tank at the temperature of operation. Thus the corrosion loss in two weeks in a test sample of stainless steel immersed in such solution for such period of time was only 1.89 milligrams per square inch. The same solution, however, replacing the sodium chloride with hydrochloric acid in an amount equivalent to the HCl the corrosion at the same temperature for a like period of time was 11.71 milligrams per square inch.

The concentration of the halide salt and of the acid may be varied in wide range; for example, the halide may vary from 1% up to saturation value. The acid may be added in an amount ranging up to saturation value. Instead of orthophosphoric acid we may use meta or pyrophosphoric acid or any other acid which would preferably be non-corrosive to steel; for example, oxalic, maleic, citric, sulfanilic, formic, lactic, acetic, sulfamic, chromic, hydroxyacetic, tartaric, or thioglycolic acid. These acids may be generally termed as non-corrosive to stainless steel. They may be added in an amount to adjust the pH from about 1 or less to about 5 or 6, or used in larger amounts of, for example, from about 1% up to saturation value.

Instead of organic solvent for the attack on the organic coating composition we may use the stripping agent in an alkaline solution. Thus, for example, a potassium or sodium bromide iodide, chloride or fluoride in a solution made alkaline with KOH, NaOH, Na_2CO_3, $(NH_4)_2CO_3$ also attacks the mirror rapidly causing a separation of the organic coating material and the metallic silver film without destruction or solution of the metallic film, causing the film to separate in large strips or sheets.

EXAMPLE 3

The following three solutions were formulated in accordance with the following scheme:

An 8% solution of KI containing 10% KOH in distilled water;

An 8% solution of KCl containing 10% of KOH in distilled water;

An 8% solution of KBr containing 10% of KOH in distilled water.

Silver mirrors coated with shellac and paint were immersed in these solutions at a temperature of 160 to 170° F. and the metallic coating and the organic coating stripped off in substantially large sheets from the glass in a period ranging from about 5 to 30 minutes, when employing the KI and KBr. However, in the case of the KCl solution it required over 2 hours to accomplish the same stripping.

The halides are also active at lower temperatures as exemplified by the following:

EXAMPLE 4

An 8% by weight sodium fluoride solution in distilled water containing 10% by weight of KOH, and an 8% by weight sodium bromide solution containing 10% by weight of KOH in distilled water were employed to strip mirrors coated with shellac and paint at a temperature of 75° F.

The sodium bromide solution caused complete stripping of the mirror in less than 10 minutes, while the sodium fluoride required about 1 hour.

The concentration of the alkali and halide salt may be varied from about 1% or less up to saturation. However, it will be found that a salt concentration of from 1% to 20% and an alkali concentration of from 1% to 25% will be suitable.

Instead of using KOH or NaOH the solutions may be made alkaline by other inorganic alkalies; for example, ammonium carbonate. The following example exemplifies this method of treatment:

EXAMPLE 5

An 8% by weight of sodium bromide solution in distilled water containing also 5% by weight of ammonium carbonate, and 2% by weight of a wetting agent; for example, sodium salt of an alkyl aryl sulfonic acid was employed in stripping a silver mirror coated with a shellac and paint backing at a temperature of 167° F., and the silver mirror and the paint were completely removed from the glass in less than 30 minutes.

Instead of using an inorganic basic material, one may employ an organic base to add alkalinity to the solution. A soluble primary, secondary, or tertiary amine, or the alkenol amines may be so employed, for example:

EXAMPLE 6

A distilled water solution containing 5% by weight of KI and containing also 10% by weight of KOH and also 5% by weight of urea was employed in treating a mirror coated with shellac and paint by immersion of the mirror in the solution at a temperature of 160° F.

The mirror was stripped in 6 minutes.

The potassium hydroxide may be omitted, for example:

EXAMPLE 7

An 8% solution of sodium bromide in distilled water containing 4% by weight of triethanolamine and 2% by weight of the above wetting agent was employed as above in stripping a mirror which was coated with paint and shellac at a temperature of 166° F.

The mirror was stripped completely in less than 30 minutes.

EXAMPLE 8

A 20% by weight of sodium bromide in distilled water containing 4% by weight of hexamethylene tetramine and 2% by weight of the above wetting agent was employed to strip a mirror coated with paint and shellac at a temperature of 75° F.

The mirror was immersed in the solution and the paint was stripped from the glass in less than 30 minutes.

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 for stripping silver mirrors, which comprises immersing said mirrors in a water solution of a halide chosen from the group consisting of an alkali metal and ammonium halide at a temperature ranging from atmospheric to 200° F., and stripping the silver from the glass.

2. A process for stripping silver mirrors, which comprises immersing said mirrors in a water solution of an iodide chosen from the group consisting of an alkali metal iodide and ammonium iodide at a temperature ranging from atmospheric to 200° F., and stripping the silver from the glass.

3. A process for stripping silver mirrors, which comprises immersing said mirrors in a water solution of a bromide chosen from the group consisting of an alkali metal bromide and ammonium bromide at a temperature ranging from atmospheric to 200° F., and stripping the silver from the glass.

4. A process for stripping silver mirrors, which comprises immersing said mirrors in a water solution of a chloride chosen from the group consisting of an alkali metal chloride and ammonium chloride at a temperature ranging from atmospheric to 200° F., and stripping the silver from the glass.

5. A process for stripping silver mirrors, which comprises immersing said mirrors in a water solution of a halide chosen from the group consisting of an alkali metal halide and ammonium halide having a pH of 8 to 11 at a temperature ranging from atmospheric to 200° F., and stripping the silver from the glass.

6. A process for stripping silver mirrors, which comprises immersing said mirrors in a water solution of an iodide chosen from the group consisting of an alkali metal iodide and ammonium iodide having a pH of 8 to 11 at a temperature ranging from atmospheric to 200° F., and stripping the silver from the glass.

7. A process for stripping silver mirrors, which comprises immersing said mirrors in a water solution of a bromide chosen from the group consisting of an alkali metal bromide and ammonium bromide having a pH of 8 to 11 at a temperature ranging from atmospheric to 200° F., and stripping the silver from the glass.

8. A process for stripping silver mirrors, which comprises immersing said mirrors in a water solution of a chloride chosen from the group consisting of an alkali metal chloride and ammonium chloride having a pH of 8 to 11 at a temperature ranging from atmospheric to 200° F., and stripping the silver from the glass.

9. A process for stripping silver mirrors which comprises immersing said mirrors in a water solution of a halide chosen from the group consisting of alkali metal halide and ammonium halide, and containing also an acid chosen from the group of acids which is non-corrosive to steel, consisting of ortho-phosphoric acid, metaphosphoric acid, pyro-phosphoric acid, oxalic acid, maleic acid, citric acid, sulfanilic acid, formic acid, lactic acid, acetic acid, sulfamic acid, chromic acid, hydroxyacetic acid, tartaric acid, and thioglycolic acid, said solution having a pH of from less than 1 to about 6 at a temperature ranging from atmospheric to 200° F., and stripping silver from the glass.

10. The process of claim 9 in which the halide is an iodide.

11. The process of claim 9 in which the halide is a bromide.

12. The process of claim 9 in which the halide is a chloride.

13. A process for stripping silver mirrors which comprises immersing said mirrors in a water solution having a pH from about 1 to about 11 and containing halide ions and an ion taken from the group of the alkali metals and ammonium, at a temperature ranging from atmospheric to 200° F., and stripping the silver from the glass.

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