United States Patent

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ABSTRACT: A mirror is made by depositing silver on a glass plate by chemical reduction of silver nitrate, covering the silver film with a protective copper layer deposited from a copper sulfate solution by means of a finely divided less noble metal, and by passivating the copper coating by contact with a solution of chromic acid, a chromate, or a dichromate.
METHOD OF MAKING A MIRROR

BACKGROUND OF THE INVENTION

The invention relates to mirrors having a reflecting silver surface protected by a copper coating, and particularly to an improvement in mirrors whose copper coating is formed by reduction of a copper sulfate solution by means of a metal less noble than copper.

A reflecting silver film is readily deposited on plate glass, transparent plastic, or other solid, inert, transparent substrates by contacting a surface of the substrate with a solution of a silver salt containing a reducing agent. A more uniform and better adhering deposit is obtained if the surface to be coated is first activated. Although the silver film so produced is very thin, it is mechanically and optically adequate for a second surface mirror when protected by a coating of metallic copper.

Copper coatings can be formed by electrodeposition but a simpler chemical deposition method has been disclosed by Meth in U.S. Pat. No. 2,664,363, 2,720,487, and 2,768,944. A copper layer having a thickness of 200 μ or even more is formed on the silver film by contact with a copper sulfate solution in which a metal less noble than copper is dispersed. The deposition rate is highest if the copper is deposited from an acidic solution.

Silver mirrors covered with a copper layer by the chemical method outlined above have been found to corrode more readily than otherwise similar mirrors in which the copper coating is formed by electrodeposition. Even relatively heavy copper coatings produced by the above chemical method are prone to form corrosion pits even when carefully rinsed to remove all soluble electrolytes from the copper surface. Corrosion is even more rapid if the copper coating is not rinsed with extreme care.

An object of the invention is the provision of a mirror having a reflecting silver film protected by a chemically deposited copper coating which has improved corrosion resistance. Another object is the provision of a method for producing such a mirror which does not require time-consuming rinsing of the copper coating.

SUMMARY OF THE INVENTION

It has now been found that the corrosion resistance of a mirror having a reflecting silver surface protected by a coating of copper deposited on the silver by reduction of copper sulfate by means of a dispersed metal less noble than copper can be greatly improved by contacting the exposed surface of the copper coating with an aqueous solution of chromic acid or of a water soluble chromate or dichromate.

Copper coatings as thin as 40 μ adequately protect a mirror of the invention against corrosion if passivated by the chromating treatment. Rinsing before or after the treatment is not critical nor even useful. Good correlation has been found between atmospheric corrosion tests of mirrors of the type described and accelerated tests of varying severity which will be referred to hereinafter as test I, test II, and test III.

In test I, the exposed copper surface of the finished mirror is sprayed with distilled water for a few seconds and dried. In test II, the copper coating is left in contact with 30 g/l. sodium chloride solution for 48 hours at room temperature. In test III, the copper surface is covered for five minutes with a filter paper freshly impregnated with an aqueous solution of 60 g/l. sodium chloride, 10 g/l. potassium ferricyanide, and 1.2 ml/l. concentrated ammonium hydroxide solution. After exposure to the corrosive medium, the corrosion behavior of the mirror in the atmosphere can be predicted with good accuracy from the number of pin holes visible in the reflecting silver surface under a low power microscope.

DESCRIPTION OF PREFERRED EMBODIMENTS

The following examples are further illustrative of the method of the invention.

EXAMPLE 1

A glass plate was thoroughly cleaned and ultimately rinsed with distilled water. A surface of the plate was then activated by brief contact with a 0.3% solution of stannous chloride. It was then silvered by pouring a freshly prepared 2:1 mixture of a silver salt solution and of a reducing solution over the plate at a rate of 5 ml per dm² glass surface. The silver salt solution contained 25 g/l. silver nitrate and 36 g/l. ammonium hydroxide. The reducing solution contained 10 g/l. cane sugar and 1.4 g/l. tartaric acid. The silver layer formed had a thickness of 55 μm.

It was coated with copper by simultaneous spraying with a solution of 100 g/l. copper sulfate crystals and 10 g/l. ammonium persulfate and with a dispersion of 9 g/l. zinc powder in a volume ratio of 25 ml/dm² to 27 ml/dm², whereby a copper coating 87 μm thick was formed. The zinc particles and used passed a 300 mesh screen.

The freshly copper-coated solution was not rinsed with water but was directly dipped for five seconds in a solution of 0.5 g/l. chromium trioxide or chromic acid. After withdrawal from the chromating solution, the finished mirror was air-dried without rinsing. Its appearance was not affected by the chromating treatment.

When dry, it was subjected to test III, the most severe of the three accelerated corrosion tests described, and not a single pin hole or corrosion pit was found in the reflecting silver film.

When a mirror was prepared in the same manner by silvering a glass plate and coating the silver film with copper, and when the exposed face of the copper layer was thereafter carefully rinsed with an ultimate 20 second spray of distilled water, the test III of the dry mirror produced 34 corrosion pits per square decimeter.

Mirrors of the invention prepared as described above similarly withstood tests II and I, and exposure to an ambient corrosive atmosphere for two days without a single failure. The copper remained bright in the atmosphere. Under the same conditions, a mirror not chromated but carefully rinsed showed 18 pits per dm² after 6 hours of immersion in 30 g/l. sodium chloride solution. The corrosive atmosphere mentioned above caused the untreated copper layer to turn black but no failures were found in the silver layer. 100 Corrosion pits were found after two days in the silver film of the mirror which had not been chromated after 5 seconds spraying with distilled water and drying in the atmosphere.

EXAMPLE 2

A carefully cleaned glass plate was activated by contact with a 0.1% solution of stannous chloride and silvered by flooding at a rate of 5 ml/dm² with a freshly prepared 2:1 mixture of a silver salt solution prepared from 18 g/l. silver nitrate, 32 g/l. ammonium hydroxide, and 14 g/l. sodium hydroxide, and a reducing solution containing 10 g/l. cane sugar and 1.4 g/l. tartaric acid. The silver film produced had a thickness of 50 μ. It was then sprayed simultaneously with 30 ml/dm² of each of an aqueous solution containing 120 g/l. CuSO₄, 5H₂O and 7 g/l. sulfuric acid and a dispersion of 10 g/l of iron powder (passing a 300 mesh screen) in a liter water. The copper coating had a thickness of 94 μm, and was sprayed without an intermediate water rinse at a rate of about 3 ml/dm² with a potassium dichromate solution containing chromium equivalent to 1 g/l. CO₃. The mirror was then dried immediately. It withstood test III without showing a single corrosion pit in the silver film. It similarly passed test I and II without a single failure, and the brightness of the copper coating was not reduced by exposure to the aforementioned corrosive atmosphere.

Mirrors produced by silvering and copper coating in the same manner, but thereafter rinsed and dried showed 20 corrosion pits per dm² after test III, 50 pits after test II shortened to 6 hours immersion, and 40 pits after test I. The copper layer was blackened by the atmosphere.
EXAMPLE 3

A thoroughly cleaned and rinsed glass plate was activated with a 0.05% stannous chloride solution and thereafter silv-ered by flooding with a 2:1 mixture of a silver salt solution containing 20 g./l. silver nitrate, 35 g./l. ammonium hydroxide, and 15 g./l. sodium hydroxide, with a reducing solution of 10 g./l. cane sugar and 1.4 g. tartaric acid. The silver film produced had an average thickness of 54 mg.

It was coated with 120 mg copper by simultaneous spraying with 40 ml. per dm.² each of a solution containing 100 g./l. CuSO₄.5H₂O and 15 g./l. ammonium persulfate, and of a dispersion of 9.3 g. zinc powder (passing a 300 mesh screen) in one liter water. The freshly deposited copper coating was not washed, but the mirror was dipped at once for three seconds in a solution of sodium chromate containing 2 g./l. CrO₃ equivalent. It withstood all corrosion tests as described in examples 1 and 2.

Mirrors prepared in the same manner to have a silver film and a copper coating of the thicknesses indicated, but washed after copper deposition and thereafter dried, showed 20 corrosion pits per dm.² in test III, 40 pits after a test II shortened to 6 hours of immersion, and 30 pits in test I. The copper coating turned black upon 2 days' exposure to the corrosive at-mosphere.

While the specific silvers, copper coating and chromating conditions used in the specific examples hereinafore are characteristic of good present practice, many of the condi-tions employed need not be maintained strictly, and they may be varied within rather wide limits without loss of all the ad-vantages of this invention.

While glass is the preferred transparent substrate, smooth surfaces of other inert, transparent materials have been success-fully silvered before and copper-backed second surface silver mirrors produced on various plastics or on mica fully benefit from the chromating treatment of this invention. Ac-tivating treatments with nucleating agents other than stannous chloride are well known to those skilled in the art and may be substituted for the specifically disclosed method without af-fecting the results achieved. When stannous chloride is used, it should be present in the activating solution in a preferred con-centration of 0.01 to 1.0 percent.

The silversing of glass and plastics is a well developed art. The silver film need not be deposited by chemical reduction of a silver salt from its aqueous solution but may be formed by vacuum deposition in a known manner. If an ammoniacal silver nitrate solution provides the silver salt in the reduction method, the concentration of silver nitrate should be about 5 to 25 g./l., and that of ammonium hydroxide 10 to 50 g./l. Equivalent amounts of other silver salts may be substituted for the nitrate.

The reducing agent should be used in an amount sufficient to precipitate from the solution approximately 30 to 60% of the silver present therein as a soluble compound. Rochelle salt, saccharides other than sucrose, and formaldehyde are merely representative of the wide range of reducing agents which have been used for the same purpose heretofore, and are equally applicable in the method of this invention.

As has been disclosed in the aforementioned patents, cadmium, nickel, cobalt and chromium may be substituted for the zinc and iron powders described in the examples. It has further been found that the same or closely similar effects are produced by tungsten powder, molybdenum powder, or manganese powder, and by finely dispersed alloys of the several metals mentioned. About 6 to 12 grams of the fine metal powders can be kept adequately dispersed in a liter of water by mechanical agitation. The concentration of the metal disper-sion is chosen so that it may be sprayed on the silver surface at a rate of 20 to 60 ml./dm².

The copper sulfate solution may contain 50 to 240 g./l. copper sulfate crystals (CuSO₄.5H₂O) and should contain 5 to 20 grams of an acidic solution agent. The use of sulfuric and phosphoric acid has been disclosed in the above-identified patents, but tartaric acid, oxalic acid, formic acid and many other acids varying in their dissociation rate between the values for sulfuric acid and the mentioned organic acids have been found similarly effective. Good results have also been obtained with sodium salts, ammonium persulfate being par-ticularly useful in producing good mirrors with a minimum thickness of copper.

The ratio of copper sulfate and reducing metal in the mix-ture applied to the silver surface should be such that the copper sulfate is present in an amount five to ten times the equivalent of the reducing metal. Thus, a large excess of copper sulfate remains in the solution after the reducing metal is completely spent. A copper layer 45 to 100 mg is quickly formed, and heavier coatings may be prepared, as has been shown above.

The chromating solution may contain chromic acid or solu-bile chromates or dichromates. The alkali metal and ammoni-um chromates and dichromates are most conveniently available and are preferred if free chromic acid is not used. While the chromating solution produces useful results at concentra-tions between 0.01 and 0.8 g./l. chromium trioxide, or the corresponding amount of chromate or dichromate, concentra-tions of less than 0.1 g./l. are too slow to be practical, and nothing is gained by increasing the concentration beyond 20 g./l. while drop-out losses of CrO₃ values are unnecessarily increased. The advantages obtained by concentrations of more than 2 grams per liter are quite small, and the preferred concentration of CrO₃ or its equivalents is thus 0.1 to 2 grams per liter. It will be appreciated that one mole of sodium dichromate is the equivalent of two moles of chromium triox-ide for the purpose of this invention.

The chromating solution should be free from significant amounts of strong acids such as sulfuric acid, hydrochloric acid, or nitric acid. The concentration of strong mineral acid, if any, should be not more than to make the chromating solu-tion 0.01 N with respect to the acid. Nitric acid is particularly detrimental when present in excessive amounts.

The necessary time of contact between the copper deposit and the chromating solution is short, one second being generally adequate. While there does not seem to be a critical upper limit to the chromating time, nothing is accomplished by extending the chromating treatment beyond a few seconds, and the copper layer may be attacked by the more concen-trated chromium oxide, chromate, or dichromate solutions. The treatment should therefore not usually be prolonged beyond 300 seconds. The method of application may be chosen freely, dipping and spraying being usually most con-venient. Spraying with 5 to 50 ml./dm² is normally preferred.

The copper coating may be washed with water prior to chromating and also after chromating, but the washing is not necessary and only adds to the cost of the method. The freshly deposited copper layer may be chromated at once while still wet with the mixture employed in forming the copper deposit.

What is claimed is:

1. In a method of making a mirror in which a smooth surface of a solid, inert, transparent substrate is silvered, and the silver film on the substrate is further coated with a protective layer of copper by reduction of an acidic copper sulfate solution by means of a finely divided metal less noble than copper, the im-provement which comprises contacting the exposed surface of said protective layer with a dilute aqueous solution essentially consisting of water and of chromic acid, a water-soluble chro-mate, or a water-soluble dichromate, at ambient temperature, said solution containing an amount of chromium equivalent to 0.01 to 80 grams per liter chromium trioxide, and said ex-posed surface being contacted with said aqueous solution for not substantially less than one second.

2. In a method as set forth in claim 1, said exposed surface being contacted with said aqueous solution after the coating of said silver film with said protective layer without intermediate rinsing of the exposed surface with water.
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3. In a method as set forth in claim 2, said exposed surface being contacted with said aqueous solution while still carrying an amount of said copper sulfate solution.

4. In a method as set forth in claim 3, said aqueous solution containing an amount of chromium equivalent to not more than 20 grams per liter chromium trioxide.

5. In a method as set forth in claim 4, said aqueous solution being substantially free from acid having a strength similar to that of sulfuric acid.

6. In a method as set forth in claim 4, said aqueous solution being a solution of an alkali metal salt or of an ammonium salt of chromic or dichromic acid.