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DEPOSITION OF GOLD FILMS

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11 Claims

This invention relates to the deposition of gold films on metallic and nonmetallic surfaces, and more particularly to a chemical reduction method for producing said films, to solutions used in said method, and to gold-plated articles produced by said method.

The deposition of gold films on glass and other non-metallic substrates by a chemical reduction method involving generally the reduction of a gold compound to metallic gold by a reducing agent has been described in a 1953 work by Samuel Wein entitled Gold Films (Metallic Coatings on Non-Metallic Materials, vol. 5) and published by the U.S. Department of Commerce, Office of Technical Services. The rates of film deposition in many of these methods have been relatively slow, requiring from five minutes to twenty-four hours of immersion in the plating solutions. Other methods involve relatively complicated process steps. Still other methods have required elevated temperature heating of the substrate or of the solution. In another method involving the spraying of gold films on glass, the exposed surface of the film, or the side not in contact with the glass, has a dull, brownish appearance. The rate of gold deposition in this method is slow, and the dull appearance of the exposed gold surface prevents its use for other applications.

In contrast, the present invention provides for a relatively fast, simple, and economical method of depositing gold films on both metallic and nonmetallic surfaces. Only conventional apparatus is required, and the method may be carried out at ambient temperatures. The films deposited by the present method are continuous, adherent, and bright, making them suitable for many different applications in industry.

According to the present invention, gold films are produced on various metallic and nonmetallic surfaces by contacting said surfaces with a solution containing a gold salt and a gold complexer and another solution containing hydrazine as the reductant for the gold. Upon mixing of the two solutions, a film of bright metallic gold is deposited on the surface. Many different surfaces may be coated by the method of the present invention. They include metals, glass, plastics, ceramics, and painted surfaces. Metals such as silver, copper, and iron can be coated directly by the method of the present invention. Other metals, such as magnesium and aluminum, which are too active electrochemically to receive the gold film directly, may be coated by the present method after providing an anodic oxide or other suitable barrier coating, such as lacquer.

Unlike autocatalytic chemical reduction processes, the present method does not require a catalytic surface for the deposition of the gold. All that is required is that the surface be clean and free of hydrophobic substances so that wetting can occur. For the cleaning of glass and other surfaces, ordinary household cleansers and detergents have been found to be suitable. To increase adherence of the gold film, the surfaces may be abraded, chemically etched with a suitable solvent, or otherwise treated to increase micro roughness or polarity.

More specifically, the present gold solution is prepared by dissolving in water, a gold salt, such as gold chloride, gold bromide, sodium gold thiosulfate, or other soluble

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salt in a concentration in excess of about 10^{-3} moles per liter. It has been found that the concentration of the free gold ions to be reduced, in the form of the aquo-coordinated gold ion which is presumably $\text{Au}(\text{H}_2\text{O})_4^{+++}$, should not exceed 10^{-16} gram ions per liter. The gold in excess of this concentration is complexed by a suitable complexer or ligand. These ligands usually contain a nitrogen or oxygen donor atom and include alkali metal carbonates, alkali metal hydroxides, ammonia, and aliphatic amines containing from 1 to about 8 carbon atoms and from 1 to about 5 nitrogen atoms. These complexers may be used singly or in combination with each other. The pH of the gold metal solution may range from about 5 to about 11, with a near neutral condition being preferred.

Table I below shows some examples of gold metal solutions which can be used in the method of the present invention. All of these solutions may be used for rapidly depositing a specular film onto glass to produce high quality gold mirrors. In addition, the solutions indicated with an asterisk (*) may be used to coat opaque articles. The coatings produced thereon are extremely bright and decorative, particularly when the surface of the article is smooth.

TABLE I.—GOLD SOLUTIONS

Gold salt, moles per liter	Ligand, moles per liter	pH
0.001	Ammonium carbonate, 0.005*	8
0.005	Ammonium hydroxide, 0.005*	7
0.01	Sodium hydroxide	11
0.05	Methylamine, 0.2	7
0.02	Ethylamine, 0.04	7
0.005	Ethylenediamine, 0.015*	6
0.02	Diethylenetriamine, 0.04*	7
0.02	Triethylenetetramine, 0.04*	7

The gold solutions containing ethylenediamine are the preferred solutions since they are the most stable and may be stored for long periods of time without the formation of appreciable quantities of elemental gold or insoluble gold compounds. These solutions preferably contain from about 0.005 to about 0.2 mole per liter of a gold salt and ethylenediamine in a molar ratio of the ethylenediamine to gold equal to about 2, or greater. The pH of these solutions is preferably maintained at from about 6 to about 8.

In preparing the gold solutions, it is important that the ingredients be mixed in the prescribed manner so as to avoid the formation of insoluble precipitates. In accordance with the present invention, the gold salt, for example gold bromide, is first dissolved in water and then neutralized with sodium hydroxide or some other soluble alkali metal hydroxide. The ligand, for example diethylenetriamine, is separately diluted with water and then neutralized with an acid such as hydrobromic acid. The gold salt solution and the ligand solution are then mixed to form a final gold solution containing free and complexed gold ions in the concentrations previously specified.

The present reductant solution may contain from about 0.1 to about 6 moles per liter of hydrazine and from 0 to about 2 moles per liter of an alkali metal hydroxide. For spray applications of the gold and reductant solutions, the reductant solution preferably contains from 2 to 5 moles per liter of hydrazine and less than 1.5 moles per liter of alkali metal hydroxide.

Adjuncts such as wetting agents, brighteners, and pH buffers may also be added to either the gold metal solution or to the reductant solution without departing from the scope of this invention.

In the preferred form of the present invention, the gold solution and the reductant solution are sprayed simultaneously onto the surface of the article to be coated. The

spraying may be done at ambient temperatures and with spray equipment of the type commonly used for applying paints. These include airless spray equipment or atomizers which employ air or other gases such as fluorocarbons and hydrocarbons. Preferably, the surface of the article to be plated is initially wetted with the reductant solution before the two solutions are simultaneously sprayed on the surface. Pressures in the order of 20 to 30 pounds per square inch may be used in pneumatic atomizing spray guns, and the sprays may be applied from a distance of about one foot from the article. As in conventional spraying methods, it is desirable that the present spraying operation be carried out in well ventilated areas.

The thickness of the present gold coatings increases with the flow rate and time of spray. However, essentially any desired coating thickness may be obtained. As with other chemical reactions, the deposition rate increases with the concentration of the reactants and the temperature. The present films deposit at rates of 15 microinches per minute or more at ambient temperatures. Thus, opaque coatings can be sprayed in a fraction of one minute.

The efficiency of the present spray method is relatively high. For example, despite the rapid flow of solutions over the substrate, it has been found that over half of the dissolved gold that is sprayed on a glass surface becomes deposited. Thin films can therefore be applied quite economically by this method without resorting to the usual industrial practice of recovering unused gold residues. The spray method also lends itself well to the coating of large parts, such as passive satellites, as well as miniature parts.

In addition to the simultaneous spraying of the gold and reductant solutions, the two solutions may also be flowed simultaneously over the article in such manner that mixing of the solutions takes place at the article surface. Another method of applying the coating in accordance with the present invention is to immerse the article in the gold solution and then add the reductant solution, with stirring, to the gold solution. The following example is illustrative of this latter method.

A neutral gold solution was prepared which contained 0.05 mole per liter of gold chloride and 0.1 mole per liter of ethylenediamine. A plate of clean borosilicate type glass was immersed therein. A reductant solution containing 0.6 mole per liter of hydrazine and 0.03 mole per liter of potassium hydroxide was prepared and added with stirring to an equal quantity of the gold solution. Gold deposition on the glass started within 15 seconds and was complete within several minutes at ambient temperature (22° C.).

The exact nature of the present process is not clearly understood. Apparently, the two reactants meet at the substrate surface and form very tiny gold crystals. These particles form on the substrate and adhere to it. The reaction conditions are such that additional gold particles nucleate and form rather than continue the growth of crystals initially deposited. The newly formed particles continue to adhere to one another and to the substrate, indicating that surface energy may play a role in this reaction. In any event, the net result is an unexpectedly bright, highly reflective film of fine, crystalline gold. Even at 400,000 magnification, the film surface is extremely smooth.

Gold films deposited by the method of the present invention have many useful properties. For example, the electrical resistivity of the present films was measured by the two-point and four-point probe technique on films deposited on frosted glass squares by the simultaneous spraying of a gold solution and reductant solution prepared as follows: 50 ml. of 0.2 molar gold chloride solution were added to 700 ml. of water and a sodium hydroxide solution was added until the acidity had been neutralized. 1.5 ml. of ethylenediamine were added to

50 ml. of water and then hydrochloric acid was added until the alkalinity had been neutralized. The first solution was added to the second solution and the resulting gold solution was thoroughly mixed after being brought to one liter with water. The reductant solution was prepared by mixing 50 ml. of one molar sodium hydroxide with 100 ml. of 20 molar hydrazine, and then diluting to 1 liter with water. The gold and reductant solutions were simultaneously sprayed on seven glass plates. The film thicknesses ranged from 1300 to 6200 Angstrom units based on weight measurements. The average resistivity of these coatings was 6.4 microhm-cm. as measured by the four-point probe method. This can be compared with the accepted value of 2.4 microhm-cm. for massive gold at 20° C. Since the experimental resistivity values are based on the apparent surface area, they would actually be somewhat less and in closer agreement with the accepted value if a correction is made for the roughness of the frosted glass. Thus, it appears that the electrical resistivity of the present gold films is close to the value for bulk gold and that these films would be useful as conductors, counter electrodes, and contacts.

The optical properties of the present gold films, or more specifically the capacity to absorb and emit radiant energy of certain wave lengths, were measured on films of about 2000 Angstrom units thickness deposited by spraying on anodized coupons of 6061 aluminum alloy and HM21 magnesium alloy. The gold solutions and reductant solutions were prepared in a similar manner as that described for the resistivity tests. Table II below shows the optical results obtained.

TABLE II.—OPTICAL PROPERTIES OF GOLD COATING

Substrate	α_s	ϵ_{RT}	α/ϵ
Anodized aluminum.....	0.31	0.11	2.8
Anodized magnesium.....	0.35	0.12	2.9

The value for solar absorptivity, α_s , of 0.3 is normal for gold surfaces. However, room temperature emissivity, ϵ_{RT} , varies with substrate surface preparation and the nature of the deposit. (These films exhibited a matte appearance since the substrate surface was not smooth.) ϵ_{RT} can be altered as desired by such techniques as polishing the substrate surface or by modifying the spray process to deposit gold with a black appearance. These properties indicate the suitability of the present films for use in the space industry for passive thermal control surfaces, solar reflectors, and the like.

An especially useful application of the method of the present invention is the spraying of gold films on glass. It has been found that such films have a bright appearance on both the exposed and reverse surfaces. The coatings are free of imperfections and discolorations and therefore are suitable for high quality mirrors. Both the adhesion and abrasion resistance of the films deposited on glass can be considerably improved by a heat treatment cycle. Table III shows the optimum time-temperature relationship for films deposited on microscope slides made of a borosilicate glass.

Table III.—Heat treatment for gold film on borosilicate glass

Temperature, ° C.:	Time, hrs.
100	8 or more
200	2-3.5
250	1-1.5

After heat treatment, the gold films show no separation or lifting from the glass when a pressure-sensitive adhesive tape is adhered to the film and pulled off. The gold films also resist the abrasion produced by rubbing a rubber eraser over the film.

Obviously, other modifications and variations of the present invention are possible in the light of the above teachings. It is therefore to be understood that the scope

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of the present invention is to be limited only by the appended claims.

I claim:

1. A method for applying a gold film to a surface which comprises simultaneously spraying said surface with an aqueous gold solution containing a gold salt in an amount greater than about 10^{-3} moles per liter, free aquo-coordinated gold ions in an amount not exceeding 10^{-16} gram ions per liter, and a ligand for complexing the remainder of the gold ions in solution, and with an aqueous reductant solution containing from about 0.1 to about 6 moles per liter of hydrazine and less than about 2 moles per liter of an alkali metal hydroxide, said solutions reacting to deposit a film of gold on said surface.

2. A method according to claim 1, wherein the gold salt is selected from the group consisting of gold chloride, gold bromide, and sodium gold thiosulfate.

3. A method according to claim 1, wherein the gold complexer is selected from the group consisting of an alkali metal carbonate, ammonia, an alkali metal hydroxide, and an aliphatic amine containing from 1 to about 8 carbon atoms and from 1 to about 5 nitrogen atoms.

4. A method according to claim 1, wherein the reductant solution contains from 2 to 5 moles per liter of hydrazine and less than 1.5 moles per liter of an alkali metal hydroxide.

5. A method for applying a gold film to a surface which comprises simultaneously spraying said surface with an aqueous gold solution containing from about 0.005 to about 0.2 mole per liter of a gold salt and ethylenediamine in a molar ratio of ethylenediamine to gold equal to about 2, and with an aqueous reductant solution containing from 2 to 5 moles per liter of hydrazine and less than 1.5 moles per liter of an alkali metal hydroxide.

6. A method according to claim 5, wherein the pH of the gold solution is maintained at about 6 to about 8.

7. A method for applying a gold film to a surface which comprises contacting said surface with an aqueous solution containing a gold salt in an amount greater than about 10^{-3} mole per liter, free aquo-coordinated gold ions in an amount not exceeding 10^{-16} gram ions per liter, and a ligand for complexing the remainder of the gold ions in solution, and with an aqueous reductant solution containing from about 0.1 to about 6 moles per liter of hydrazine and less than about 2 moles per liter of alkali metal hydroxide, said solutions reacting to deposit a film of gold on said surface.

8. A method for applying a gold film to glass which comprises cleaning said glass, simultaneously spraying the glass surface with an aqueous gold solution containing from about 0.005 to about 0.2 mole per liter of a gold salt and ethylenediamine in a molar ratio of ethylenediamine to gold equal to about 2, and with an aqueous reductant solution containing from 2 to 5 moles per liter of hydrazine and less than 1.5 moles per liter of an alkali metal hydroxide, said solutions reacting to deposit a continuous film of bright metallic gold on said surface, and then heating the glass surface.

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9. A method for applying a gold film to a surface which comprises simultaneously spraying said surface with an aqueous gold solution containing at least 0.001 mole per liter of a gold salt and an aliphatic amine containing from 1 to about 8 carbon atoms and from 1 to about 5 nitrogen atoms, the molar ratio of said amine to said gold salt being from 1 to 10, and with an aqueous solution containing hydrazine and less than 2 moles per liter of an alkali metal hydroxide, the molar ratio of hydrazine to gold salt being from 50 to about 1000.

10. A method for applying a gold film to a surface which comprises providing an aqueous gold solution containing at least 0.001 mole per liter of a gold salt and an aliphatic amine containing from 1 to about 8 carbon atoms and from 1 to about 5 nitrogen atoms, the molar ratio of said amine to said gold salt being from 1 to 10, providing an aqueous reductant solution containing hydrazine and less than 2 moles per liter of an alkali metal hydroxide, the molar ratio of hydrazine to gold salt being from 50 to about 1,000, mixing the gold and reductant solutions, and immediately contacting said surface with the mixture of gold and reductant solutions.

11. A method for applying a gold film to a surface which comprises providing an aqueous gold solution containing at least 0.001 mole per liter of a gold salt and an aliphatic amine containing from 1 to about 8 carbon atoms and from 1 to about 5 nitrogen atoms, the molar ratio of said amine to said gold salt being from 1 to 10, providing an aqueous reductant solution containing hydrazine and less than 2 moles per liter of an alkali metal hydroxide, the molar ratio of hydrazine to gold salt being from 50 to about 1,000, and mixing the gold and reductant solutions in the presence of the surface, whereby a gold film is deposited on said surface.

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