Patented July 8, 1952

2,602,757

UNITED STATES PATENT OFFICE

2,602,757

METHOD AND COMPOSITION FOR PRODUCING SILVER COATINGS

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No Drawing. Application April 9, 1948, Serial No. 20,117

5 Claims. (Cl. 117—47)

(Granted under the act of March 3, 1883, as amended April 30, 1928; 370 O. G. 757)

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The invention described herein may be manufactured and used by or for the Government of the United States for governmental purposes without the payment to us of any royalty thereon in accordance with the provisions of the Act of April 30, 1928 (Ch. 460, 45 Stat. L. 467).

This invention relates to the production of silver coatings on surfaces and to new reducing compositions adapted to the deposition of silver from silver salt solutions. More particularly, this invention relates to the production of electrically conductive surfaces on wax or plastic electrotype molds or other non-conducting type surfaces. Still more particularly, this invention relates to the production of continuous silver coatings on wax or plastic electro-type molds by the spray method, i. e., the method wherein a spray of a silver complex solution is co-mingled with a spray of a reducer composition.

Heretofore, surfaces or objects have been silvered by conjointly spraying against or impinging on said surfaces a co-mingled spray of a reducing agent with a silver complex solution in conventional apparatus such as that disclosed in United States Letters Patent No. 625,733, issued on May 30, 1899, to one Albert Barnes. By this technique, a silver solution such as, for example, silver ammonio nitrate, otherwise known as ammoniacal silver nitrate, is intermingled with a suitable reducing agent such as, for example, formaldehyde, as disclosed in United States Letters Patent No. 2,400,518 to Kreber et al., or alternatively, hydrazine compounds or glyoxal, as disclosed in United States Letters Patent No. 2,363,354 to William Peacock, and the mixture is immediately contacted with the surface to be coated with silver.

These methods, while reasonably satisfactory for some purposes, suffer from several disadvantages, as, for example, the deposition of the silver is relatively slow, the surfaces to be coated must first be subjected to an exhaustive cleaning treatment, in many cases, the resulting silver film is full of pinholes or tends to flake off during deposition and subsequent rinsing, particularly on surfaces which are highly polished, and also, the noxious chemicals which are employed are expensive and difficult to obtain. One alternative to these methods, heretofore proposed in United States Letters Patent No. 1,989,764, is the employment of various ethanol amines as reducing agents. These ethanol amine reducing agents suffer from the serious disadvantage of necessitating the employment of high temperatures before they have any substantially effective action

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and even then a very great length of time is necessary for the treatment, so long in fact as to preclude the utilization of the Barnes spray technique above mentioned.

Accordingly, the invention has for an object the production of adherent bright coatings of silver on any desired sub-surface such as, for example, electro-type molds of wax or plastic materials. Another object is the provision of a novel reducing composition which permits substantially instantaneous reduction of silver, and at the same time, provides a continuous adherent coating of a thickness which can be controlled substantially to any desired degree. Still a further object is the production of a synergistic reducer composition adapted for the bright deposition of metallic silver from solutions of silver complexes. Other and further objects will be apparent as the ensuing description proceeds.

These objects are accomplished in accordance with this invention wherein a continuous bright adherent coating of silver is produced on a surface by first sensitizing said surface by treatment with a solution of a stannous salt and thereafter contacting the thus-sensitized surface with a mixture of a silver complex solution and a reducer solution, said reducer solution comprising a lower aliphatic aldehyde admixed with a lower alkylol amine. In one preferred embodiment, the silver complex solution such as, for example, ammoniacal silver nitrate solution, is intermixed in the spray form with a reducer solution containing a lower aliphatic aldehyde admixed with a lower alkylol amine. Certain specific proportions of the chemicals employed have been found to yield superior results in practice, as will be more fully described hereinafter.

In general, the operating steps in carrying out this invention are simply and easily carried out. For example, an electrotype mold of wax, resin, or other plastic material is cleaned and sensitized by treatment with an alcoholic solution of stannous chloride or other stannous salt. The residual stannous salt solution is then rinsed off and the surface is ready to receive the deposit of the silver coating. An ammoniacal silver nitrate solution is prepared and then, separately, a reducer solution is prepared containing the synergistic mixture of a lower aliphatic aldehyde with a lower alkylol amine, as more fully described hereinafter. The preferred spray apparatus, of the Barnes type, for example, is then charged and the twin sprays, one of silver solution and one of reducer solution, are impinged and simultaneously intermixed and brought in contact with

the surface of the electrotype mold or other object to be silvered. The apparatus is operated similarly to the operation of the well-known paint spray gun to provide a uniform coating. Thereupon, the spray apparatus is turned off and the thus-silvered mold or other object is rinsed off and is complete and ready for use. In the electro-type mold, the silver deposit is employed as one electrode and additionally plated in the usual electroplating bath.

Suitable surfaces or objects for coating with silver in accordance with this invention include glass, metal, various waxes capable of being molded, and the natural and synthetic rubbers and resins or mixtures of the foregoing, for example, objects made of paraffin wax or other waxes such as ozokerite, montan wax, carnauba and other similar wax objects, as well as objects made of polyamides of the nylon type, many of the polymerized vinyl resins such as vinyl chloride, vinyl acetate, polystyrene, polymerized acrylates, methacrylates, polymerized silicones, co-polymers, inter-polymers and mixtures of the foregoing, cellulose esters and ethers, urea-formaldehyde polymer, phenol formaldehyde resins, and mixtures of co-polymers and inter-polymers of the same, together with fillers, plasticizers, and other softening and modifying agents. Any surface having a relatively impervious surface or made of relatively impervious material can readily be coated with silver in accordance with this invention. For electro-type work, superior results have been achieved employing a vinyl acetate-vinyl chloride co-polymer sold to the trade as "Vinylite" by the Carbide and Carbon Chemicals Corporation.

Suitable silver salts for employment in accordance with this invention include many of the silver salts and their complexes which are readily reducible in solution to liberate native silver, such as, for example, ammoniacal silver chloride, ammoniacal silver sulphate, and, preferably, ammoniacal silver nitrate solution. Other readily reducible compounds of silver can likewise be employed. However, it has been found that ammoniacal silver nitrate can be readily prepared, is stable and relatively inexpensive, and it is therefore preferred.

The silver salt solution for reduction in accordance with this invention, can be prepared in any suitable way, such as, for example, by dissolving the desired quantity of silver nitrate in water, thereafter adding ammonium hydroxide until the precipitate which first forms is just redissolved and then diluting to the desired final concentration. While a wide range of concentrations can be successfully employed, it has been found that an ammoniacal silver solution complex containing about two and one-half ounces of silver nitrate per gallon of finished solution, is entirely satisfactory. Greater concentrations up to ten ounces per gallon can be employed but are wasteful of silver, while lower concentrations tend to yield thinner films. In general, a silver nitrate concentration of from one to five ounces of silver nitrate per gallon of finished ammoniacal silver nitrate solution is preferred.

Before coating the surface with silver, it is highly desirable to sensitize the surface by treatment with a solution of a stannous salt. In this invention, an entirely effective cleaning of the surface to be coated is achieved simultaneously with sensitization by rinsing the plastic or other surface to be coated with an alcoholic solution of stannous chloride or other stannous salt soluble in alcohol. Suitable stannous salts for employment as sensitizing agents include sodium stannate, stannous sulphate, stannous fluoborate, as disclosed in United States Letters Patent No. 2,421,079 to Harold Narcus, and preferably, stannous chloride. By the employment of a solution of a selected stannous salt, for example, stannous chloride, dissolved in a suitable lower aliphatic alcohol, preferably isopropyl alcohol, the plastic or other object to be coated can be sponged, wiped, rinsed or otherwise treated so as to sensitize the surface thereof for the acceptance and retention of metallic silver, while simultaneously the surface is adequately cleaned to provide a tenaciously adherent and continuously uniform coating of silver upon subsequent deposition. While isopropyl alcohol is preferred for reasons of economy and convenience, ethanol, methanol, normal propanol and similar lower aliphatic alcohols can be employed. Preferably, the concentration of stannous chloride in the isopropanol or other selected alcohol, is chosen to be approximately 1%. At this concentration, an entirely satisfactory sensitization is secured, the solubility limits of the stannous salt in the alcohol are not exceeded, undesired hydrolysis is obviated since no aqueous medium is required, and the use of auxiliary wetting and penetrating agents is eliminated. The alcoholic stannous chloride sensitization of this invention entirely overcomes the drastic cleaning procedures heretofore considered necessary while at the same time providing a continuous and tenaciously adherent deposit of metallic silver on highly polished glass, plastic or wax and other surfaces which it is desired to coat. No roughening or other abrasion treatments of the object to be treated are required.

The reducing solution employed in accordance with this invention, is a truly synergistic composition in that the combined solution of an aliphatic aldehyde with a lower alkylol amine possesses reducing properties which are a great deal stronger and infinitely superior to the reduction of metallic silver achieved by the sum of either of the component. Suitable lower aliphatic aldehydes for employment, in the reducing solution of this invention, include acetaldehyde, propionaldehyde and, preferably, formaldehyde or glyoxal. Other suitable water soluble mono- or di-aldehydes can be employed, but as stated, it is preferred to employ glyoxal or formaldehyde. Of these latter two, glyoxal is preferred in that it operates in a highly satisfactory manner while at the same time is much more convenient for workmen to handle. The glyoxal or other selected aldehyde is mixed with water and with the selected lower alkylol amine to make the finished reducing composition.

Suitable lower alkylol amines for employment in accordance with this invention include morpholine, ethylmonoethanolamine, ethyldiethanolamine, diethylethanolamine, monoethanolamine, diethanolamine, and preferably, triethanolamine. Triethanolamine constitutes a preferred lower alkylol amine for employment in accordance with this invention since it is inexpensive, yields somewhat better silver films than the others, provides a more neutral reducer solution when mixed with the selected aldehyde, and apparently has a greater stabilizing action on the finished reducing solution when admixed with glyoxal or other selected lower aliphatic aldehyde. It also interacts more slowly with the aldehyde selected. In preparing the reducer

composition for employment in accordance with this invention, the glyoxal or other selected lower aliphatic aldehyde is mixed with a suitable quantity of water and thereafter the desired quantity of triethanolamine or other selected lower alkylolamine, is incorporated in the solution. The order of mixing is unimportant to the final composition, however. A suitable quantity of lower aliphatic aldehyde in the reducer composition is from 1% to 10% by weight, although it is preferred to employ a somewhat more restricted proportion of formaldehyde, glyoxal or other lower aliphatic aldehyde, preferably within about 0.5% to 5.0% by weight of the total amount of reducer solution.

A suitable quantity of triethanol amine or other lower alkylol amine for admixture with the solvent and the glyoxal or other lower aliphatic aldehyde is from .02 to 2.0% by weight of lower alkyl amine such as triethanolamine. Preferably however, for superior results the quantity of alkylol amine in the reduced composition is maintained within the more restricted range of from about 0.5 to 1.0% by weight based on the total composition.

In the practice of this invention the following example is illustrative, without, however, being by way of limitation:

An electro-type mold made of a co-polymer of vinyl acetate with vinyl chloride is suitably impressed in the customary fashion. Thereafter, the plastic mold is rinsed thoroughly with a 1% by weight solution of stannous chloride in isopropanol. The thus cleaned and sensitized mold is rinsed with water and then exposed to an air-mixed spray of silver ammonio nitrate designated as solution A below, while concurrently mixing therewith in air a liquid spray of the reducing agent designated as solution B and prepared as described below. The mixed spray is directed against the surface of the mold until there results a bright adherent continuous metallic silver deposit having a thickness of about 150×10^{-6}mm., longer continued spraying produces a proportionately thicker film. The spraying is then discontinued and the resulting silver coated electro-type mold is rinsed in water and is ready for the customary electro-plating procedure. Upon electro-plating, it was found that a highly satisfactory electrically conductive surface was formed which showed no tendency to rupture during initial current surge.

Solution A is prepared by dissolving 2½ ounces of silver nitrate in about one-half gallon of water, then adding aqueous ammonia until the precipitate which first forms is redissolved and thereafter diluting the resulting mixture to a total volume of one gallon. Solution B is prepared by dissolving nine fluid ounces of 37% formaldehyde solution in about one gallon of water, adding thereto sufficient triethanolamine to make 0.6% by weight of finished solution. Alternatively, the formaldehyde component can be replaced by adding 2½% by volume of a 30% glyoxal concentrated solution to one gallon of the diluted triethanolamine solution.

It will be clear from the foregoing that there has been provided a highly desirable silver coating method and synergistic reducing composition for use therein which does not require the employment of heat or any other complicated procedure for its use. The silver deposition, in accordance with this invention, occurs substantially instantaneously and apparently is independent of the temperatures employed. No tedious and expensive cleaning procedures are necessary in accordance with this invention, and a continuous highly-adherent silver coating is produced whose thickness can be varied at the will of the operator by merely spraying for a longer or shorter time.

While we prefer to employ the spray coating technique, immersion coating can likewise be employed for such uses as, for example, the silvering of mirrors or the like. It has been observed that the silver coating in accordance with this invention provides substantially complete freedom from the usual commonly occurring pinholing.

One of the very important advantages of this invention is that the adherent deposit of silver shows substantially no tendency to flake off during deposition, rinsing or other subsequent operations. This holds true even when extremely thick deposits are applied to highly polished surfaces.

It will be apparent from the foregoing that various changes in the details disclosed will occur to one skilled in the art and, therefore, various changes can be made without departing from the spirit and scope of this invention.

What we claim is:

1. A synergistic reducer composition for the bright deposition of continuous silver coatings of controlled thickness from silver complex solutions which comprises an aqueous solution of from about 0.5 to 1.0% by weight of triethanolamine admixed with about 0.5 to 5.0% of a lower aliphatic aldehyde selected from the group consisting of formaldehyde and glyoxal.

2. A synergistic reducer composition for the bright deposition of continuous silver coatings of controlled thickness from silver complex solutions which comprises an aqueous solution of from about 0.5 to 5.0% of glyoxal admixed with from about 0.5 to 1.0% by weight of triethanolamine.

3. In a process for the production of an electrically conductive surface on a plastic electro-type mold, the steps which comprise first sensitizing such a mold by treating with a lower aliphatic alcohol solution of a stannous compound and then spraying the thus-sensitized mold with an aqueous solution of silver ammonio nitrate while co-mingling with said first spray a reducer spray solution comprising an aqueous synergistic mixture of about 0.5 to 1.0% by weight of triethanolamine having admixed therewith about 0.5 to 5.0% of a lower aliphatic aldehyde selected from the group consisting of formaldehyde and glyoxal, and then continuing said co-mingled spray treatment until a continuous adherent bright deposit of metallic silver of electro-type thickness is produced on said mold.

4. A process for the rapid production of a continuous bright adherent coating of silver on a surface of an electro-type mold which comprises first sensitizing said surface by treatment with a lower aliphatic alcoholic stannous chloride solution, and thereafter contacting said sensitized surface with an aqueous mixture of ammoniacal silver nitrate solution and aqueous reducing solution, said reducing solution comprising from about 0.5 to 5.0% by weight of formaldehyde and from about 0.5 to 1.0% by weight of triethanolamine.

5. In a process for the production of an electrically conductive surface on a plastic electro-type mold, the steps of first sensitizing such a mold by rinsing with a lower aliphatic alcohol

solution of stannous chloride, and then spraying the thus sensitized plastic mold with an aqueous solution of silver ammonio nitrate while co-mingling with said first spray a reducer spray solution comprising an aqueous synergistic mixture of about 0.5 to 5.0% by weight of glyoxal and from about 0.5 to 1.0% by weight of triethanolamine and continuing said co-mingled spray treatment until a continuous adherent bright deposit of metallic silver of electro-type thickness is produced on said mold.

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The following references are of record in the file of this patent:

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