

UNITED STATES PATENT OFFICE

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SOLUTION FOR ELECTROLYTIC DEPOSITION
OF TARNISH-RESISTING SILVER ALLOYSJames Ryder, Denver, Colo., assignor of one-half
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of Denver, Colo.No Drawing. Application February 15, 1938,
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2 Claims. (Cl. 204—43)

This invention relates to a solution for use as an electroplating bath and has for its principal object the provision of a solution which will deposit a silver alloy on the cathode of type which will resist tarnish. All commercial silver plating solutions deposit an electrolytically pure silver plate. Electrolytic silver, due to its extreme purity is more susceptible to tarnish than any alloy of silver. Therefore, silver plated ware is objectionable due to its extreme susceptibility to tarnish from exposure to the atmosphere, and to food products containing sulphur or sulphur compounds.

The electrolytic bath to which this invention is directed deposits an alloy of silver which is more brilliant and desirable than pure silver and yet which is so tarnish resistant that it might be termed tarnish proof. Articles plated by the use of this invention have been subjected to every conceivable food product and food acid and to all types of sulphur and sulphur compounds without the slightest trace of resulting tarnish thereon.

Another object of the present invention is to provide a silver electroplating bath which will deposit a bright plate on all surfaces so that all polishing and burnishing may be eliminated if desired.

A further object is to provide a silver electrolyte having all of the above noted advantages which will be economical to use; which can be used with present electroplating equipment without change; which will not require specialized training in experience; and which will be non-poisonous and absolutely safe to use.

Briefly, the preferred improved plating solution comprises the following reagents in substantially the following proportions:

Silver fluoride, AgF -----	(Troy) ounce..	3
Stannic fluoride, SnF_4 -----	do.....	2
Tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$ -----	do.....	4
Dextrose, $\text{C}_6\text{H}_{12}\text{O}_6$ -----	do.....	0.5
Uranium, $\text{U}(\text{OH})_4$ -----	do.....	2
Boric acid, H_3BO_3 -----	do.....	0.5
Water, H_2O -----	gallon..	1

The above bath is preferably prepared by first dissolving the silver fluoride and the stannic fluoride in approximately two thirds of the water, then dissolving the tartaric acid, dextrose and uranium hydroxide in the remainder of the water. The tartaric acid, dextrose and uranium solution is then added to the silver-stannic fluoride solution. The entire solution is constantly stirred and agitated during the mixing operation. The

boric acid is now added, the stirring being continued until the latter is completely dissolved.

The resulting solution is now allowed to settle for period of several hours to allow complete dissolution of and any chemical reaction that may take place, and to allow all inert matter to settle out. It is then filtered or decanted, and is ready for use in the plating tank. The admixed solution may be stored indefinitely as a stock solution.

The plating operation is the usual electroplating procedure and the tank and equipment may be of any standard or desired type. With this solution, however, insoluble anodes are employed, preferably but not necessarily of carbon. The work to be plated, of course, constitutes the cathode and the metals deposited thereon are drawn from the solution which must be replenished at suitable intervals from the stock solution to maintain the metal ion content of the bath.

The plating is done at ordinary room temperatures (70° to 80° F.) and it has been found that a current density of from 2 to 3 amps. per square foot is highly satisfactory.

The above described method for making the bath is for use when and where the fluorides of silver and tin are available for use. These salts, however, are not usually available on the market as such and it is preferred to prepare the bath from standard available chemicals as follows:

Precipitate silver hydroxide from a solution of silver nitrate by the addition of sodium hydroxide to the silver nitrate solution.

Filter the solution and recover the precipitate (silver hydroxide— $\text{Ag}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{AgOH}$).

Precipitate stannous hydroxide from a solution of stannous chloride by the addition of sodium carbonate to the stannous chloride solution.

Filter the solution and recover the precipitate (stannous hydroxide).

Precipitate uranium hydroxide from a solution of uranium nitrate by the addition of ammonium hydroxide to the uranium nitrate solution.

Filter the solution and recover the precipitate (uranium hydroxide).

Then mix the silver hydroxide and the stannous hydroxide together and digest with hydrofluoric acid, then dilute with water.

Dissolve the uranium hydroxide in a tartaric acid solution and add dextrose.

Add the uranium tartaric acid dextrose solution to the silver stannic fluoride solution and add sufficient water to ionize all ingredients, then add boric acid to the solution and stir until all of the boric acid is dissolved.

Allow the solution to stand for several hours

to allow the complete dissolution of and any chemical reaction that may take place and to allow all inert matter to settle out.

Filter, decanter or syphon off the clear liquid.

The silver fluoride salt supplies the argentic-ion (Ag^+) in the solution. The stannic fluoride salt supplies the tin-ion Sn^{++++} in the solution. The uranium hydroxide being soluble in water in the presence of an organic α -hydroxy acid (tartaric acid) gives a complex compound and supplies the uranium-ion (U^{++}) in the solution.

The dextrose is incorporated in the solution as an additional agent, its useful action is mainly to reduce treeing and cause the metals to be deposited in small crystals.

Boric acid is an additional agent incorporated to serve as a buffer to regulate the acidity of the solution.

While a preferred form of the invention has been described in some detail together with the theories which it is believed to best explain its

success, it is to be understood that the invention is not limited to the precise procedure described nor is dependent upon the accuracy of the theories which have been advanced. On the contrary, the invention is not to be regarded as limited except in so far as such limitations are included with the terms of the accompanying claims in which it is the intention to claim all novelty inherent in the invention as broadly as is permissible in view of the prior art.

Having thus described the invention, what is claimed and desired secured by Letters Patent is:

1. An electroplating solution comprising: silver fluoride; stannic fluoride; tartaric acid; uranium hydroxide; dextrose; boric acid; and water.
2. An electroplating solution consisting of 3 oz. silver fluoride; 2 oz. stannic fluoride; 4 oz. tartaric acid; and 2 oz. uranium hydroxide; $\frac{1}{2}$ oz. boric acid in solution in approximately 1 gallon of water.

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