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ELECTROLESS GOLD PLATING

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ABSTRACT OF THE DISCLOSURE

An electroless gold plating bath is provided which comprises water, a water-soluble gold cyanide complex, a water-soluble salt of a member selected from the group consisting of transitional metals, Group I–B metals, and mixtures thereof, and at least 20 grams/liter of ammonia and ammonium hydroxide calculated as NH_3. In addition, a method of electrolessly plating metallic surfaces with gold is provided which comprises immersing the metallic surfaces in the electroless plating bath hereinabove identified.

This application is a continuation of U.S. application Ser. No. 307,363, filed Sept. 9, 1963, now abandoned.

This invention relates to new and improved processes for the electroless plating of gold, to new and improved electroless gold plating baths, and to techniques for regulating or controlling the operation of such baths.

According to this invention, certain metallic and metallic coated articles may be plated with a tenacious, relatively thick, continuous, smooth, bright gold coating electrolessly, i.e., without the use of electricity, by immersion of such articles in the baths to be disclosed.

Among the metals or metal coatings that may be gold plated using this invention are copper, nickel, silver, gold, molybdenum and cobalt, with especially good results being obtained on copper, nickel and silver.

One object of this invention is to provide a bath capable of depositing a relatively thick, bright, continuous, smooth gold plate on metals or metallic coatings of the type described.

Another object is to provide means whereby spot etching or pitting of the metallic surface being subjected to electroless gold plating is substantially reduced or eliminated.

Still another object of this invention is to provide methods and techniques whereby metal or metallic coated articles are plated with a relatively thick, bright, smooth, continuous gold deposit by simple immersion in a gold containing bath and without the use of electricity.

Other objects of the invention will in part be obvious and will in part be made clear hereinafter.

The baths and the techniques of this invention are to be distinguished and are obviously distinguishable from electrolytic gold plating baths.

The instant baths and methods are also to be distinguished from displacement gold plating of the type described in Metals Finishing Guide Book, 27th edition, 1959, page 469 et seq., and gold mirroring procedures. In both of these well known prior art techniques, the gold plating desired and achieved is a few millionths of an inch in thickness. As distinguished from such described prior art procedures, plating thicknesses up to about 0.001 inch or more can be achieved by the baths of this invention. Moreover, the baths of this invention will plate gold at the rate of at least about 4 millionths of an inch per hour, and usually between about 35 and 120 millionths of an inch per hour, or even higher, for prolonged periods of time if desired. The instant baths may be used until substantially exhausted and may be replenished from time to time.

Heretofore, in attempting to gold plate metallic or metallic coated articles of the type described electrolessly, difficulty has been experienced in obtaining a continuous, uninterrupted gold deposit. As a result, unplated spots form at the plating surface and are exposed to the electroless gold baths for prolonged periods of time. As the plating operation proceeds, the unplated spots tend to dissolve or etch in the electroless gold bath, thereby forming pits which either mar or ruin the specimen. The havoc formation of such pit holes would raise in the manufacture of printed circuits, for example, will be readily apparent.

The present invention eliminates or substantially reduces this pit hole problem as will be made more clear hereinbelow.

Generally, the electroless gold plating baths of the present invention comprise, as the gold constituent, a water soluble gold complex, such as alkali or alkaline earth gold cyanide salt, e.g., potassium gold cyanide. The amount of such complex, calculated as Au, will range from about 2 to 10 grams/liter, with about 6.5 grams/liter being optimum.

A second major constituent of the bath is a water soluble salt of a transitional metal or a Group I–B metal. Preferred are the water soluble salts of the transitional metals palladium, cobalt, platinum and rhodium, including mixtures thereof, and the Group I–B metals copper and silver, including mixtures thereof. Also may be used mixtures of the salts of the transitional metals and the Group I–B metals. Among the salts of such metals may be mentioned the halides, e.g., chloride, bromide, fluoride, and iodide, sulfite, sulfate, nitrite, nitrate, phosphate, phosphite, and the like. The amount of such water soluble salts in the bath will range from about 0.1 to about 10 grams/liter; preferably between about 0.5 to 7 grams/liter.

Finally, the baths comprise, as an essential component, ammonium hydroxide in an amount greater than at least about 20 grams/liter, and usually at least 28 to 32 grams/liter, calculated as NH_3. Preferably the amount of ammonium hydroxide will range from about 55 to 65 grams/liter, calculated as NH_3, to a saturated solution, e.g., to a point where the bath is saturated with ammonia.

Bath stabilizers may also be added.

Rochelle salts, the sodium salts (mono-, di-, tri- and tetra-sodium salts) of ethylenediaminetetraacetic acid (EDTA), gluconic acid, gluconates, and triethanolamine are preferred as stabilizing agents, but commercially available glucono-δ-lactone and modified-ethylenediaminetetraacetates are also useful, and in certain instances give even better results than the pure sodium ethylenediaminetetraacetate. One such material is Glyco Products "Tetrine M." The quantity of such stabilizers may range up to 100 grams/liter or higher.

Also may be added, if desired, up to about 100 ml./liter of 37% formaldehyde solution, or an equivalent amount of a formaldehyde solution of different concentration; up to about 10 grams/liter of alkali citrate, such as sodium or potassium citrate; up to about 100 grams/liter of alkali hypophosphite, such as sodium or potassium hypophosphite.

Typical examples of gold plating baths produced in accordance with this invention are tabulated in Table I.

TABLE I

Bath No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Potassium gold cyanide (as Au) (g./l.)	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5	6.5
Sodium citrate (g./l.)				30	30	30	30	30	30	30		30	30		30	30	30	
Tetrasodium (EDTA) (g./l.)								20	20	10	20	10				20	20	
Palladium chloride (g./l.)	5	4	105	2	2	2	2	2	2	2	2	4						
Ammonium hydroxide (28% solution) (ml./l.)	500	500	500	500	500	500	150	500	50	450	450	500	500	500	500	500	500	500
Cobalt chloride (g./l.)															2			0.5
Cupric chloride (g./l.)													2	2				1
Silver nitrate (g./l.)																2	0.5	
Formaldehyde (37%) (ml./l.)				10														
Sodium hypophosphite (g./l.)					10								30	30	30			

In using the baths, the metallic or metallic coated article to be gold plated is immersed in the bath, and permitted to remain therein until a deposit of desired thickness is achieved. Although the baths may be run between about 35° and 90° C., best results are achieved in the temperature range of about 70° to 80° C.

Surfactants in an amount of less than about 5 grams/liter may be added to the baths disclosed herein.

Operating efficiency of the baths may be improved by the addition of surfactants in an amount of less than about 5 grams/liter. Typical of suitable surfactants are organic phosphate esters, and oxyethylated sodium salts. Such surfactants may be obtained under the trade names Gafac RE610 and Triton QS–15, respectively.

Certain of the baths of Table I were used to plate copper. The deposition data for these runs is tabulated in Table II.

What is claimed is:

1. An electroless gold plating bath comprising water, a water soluble gold cyanide complex, a member selected from the group consisting of water soluble salts of palladium, cobalt, rhodium, platinum, copper and silver, including mixtures of the foregoing, and at least about 20 grams/liter of ammonia and ammonium hydroxide, calculated as NH_3.

2. The bath of claim 1, wherein the ammonium hydroxide content of the bath is at least about 28 grams/liter, calculated as NH_3 and wherein said member is selected from the group consisting of water soluble salts of palladium, cobalt, rhodium, platinum and copper, including mixtures thereof.

3. The bath of claim 2 wherein the ammonia and ammonium hydroxide content is between about 55 and 65 grams/liter, calculated as NH_3.

TABLE II

Bath No.	[1] 1	[1] 4	[1] 5	[1] 6	[2] 7	[1] 8	[3] 9	[1] 10	[1] 11	[4] 12	[4] 13	[4] 14	[4] 15	18
Rate	120	88	74	100	52	16	86	72	80	81				4
Temp., ° C.	78	80	80	80	70	35	70	77	77	77	70	70	70	80

[1] Bright deposit. [2] Black specks formed. [3] Deposit full of black holes. [4] Bright deposit but thin.

As will be clear from Table II, where less than the minimum amount of ammonium hydroxide called for herein was maintained in the baths, black specks or pits formed, and the deposit was not satisfactory. See Baths 7 and 9. Where the ammonium concentration was maintained above the minimum values described herein, good bright gold deposits were obtained, with substantial elimination of the black pits.

To insure elimination of pit holes in operating the baths described herein, ammonia is fed to the bath either periodically or continuously to maintain the ammonium hydroxide content above the minimum levels disclosed herein.

To demonstrate the importance of maintaining the ammonium hydroxide concentration above the minimum levels described herein, two 60 gallon baths having the approximate formula of Bath 6, Table I, were prepared, and operated 20 hours a day to plate gold on copper specimens. The first bath was operated without replenishment of NH_4OH. After about 4 hours of operation, it was noted that black specks began to form in the specimens, and continued use of the bath could not be tolerated. The ammonium hydroxide content of the second bath was maintained by bubbling ammonia through the bath at a rate of about 2 pounds/hour. After the end of three days, the bath was in good operating condition, and the deposits were bright and continuous, with no evidence of pits or black specks in the deposit.

Prior to plating, the metallic surfaces should be thoroughly cleaned, degreased and/or deoxidized, as is well understood in this art.

The invention in its broader aspects is not limited to the specific compositions, steps and methods described, but departures may be made therefrom within the scope of the accompanying claims without departing from the principles of the invention and without sacrificing its chief advantages.

4. An electroless gold plating bath consisting essentially of water; a water soluble gold cyanide complex, 2–10 grams/liter calculated as Au; a member selected from the group consisting of water soluble salts of palladium, cobalt, rhodium, platinum, copper, and silver, including mixtures thereof, from 0.1 to 10 grams/liter; and ammonium hydroxide; the amount of ammonium hydroxide calculated as NH_3 being bteween about 20 grams/liter and that amount required to saturate the bath.

5. A method af electrolessly gold plating metallic surfaces which comprises immersing the metallic surface in a bath comprising water, a water soluble gold cyanide complex, a member selected from the group consisting of water soluble salts of palladium, cobalt, rhodium, platinum, copper and silver, including mixtures thereof, and at least about 20 grams/liter of ammonium hydroxide, calculated as NH_3 and maintaining said amount of ammonium hydroxide in said bath while electrolessly plating said gold.

6. A method of electrolessly gold plating metallic surfaces which comprises immersing the metallic surfaces in a bath containing water, a water soluble gold cyanide complex, a member selected from the group consisting of water soluble salts of palladium, cobalt, rhodium, platinum, copper and silver, including mixtures thereof, and at least 28 grams/liter of ammonium hydroxide, calculated as NH_3 and maintaining said amount of hydroxide by bubbling ammonia into said bath.

7. The method of claim 6 wherein the ammonium hydroxide content is about 55 to 65 grams/liter calculated as NH_3 wherein said member is selected from the group consisting of water soluble salts of palladium, cobalt, rhodium, platinum and copper and mixtures thereof.

8. A method of electrolessly gold plating metallic surfaces which comprises immersing the article having metallic surfaces in a bath comprising water; a water soluble gold cyanide complex, 2–10 grams/liter calculated as Au;

a member selected from the group consisting of water soluble salts of palladium, cobalt, rhodium, platinum, copper and silver, including mixtures thereof, from 0.1 to 10 grams/liter; and ammonium hydroxide, the amount of ammonium hydroxide being between about 20 grams/liter and that amount required to saturate the bath and maintaining said amount of ammonium hydroxide in said bath during said electroless gold plating.

9. The method of claim **8** wherein ammonia gas is bubbled through the bath during the plating operation to maintain the recited ammonium hydroxide concentration.

10. An electroless method of gold plating metallic surfaces comprising immersing the surfaces in a bath comprising water, a water soluble gold cyanide complex and a member selected from the group consisting of water soluble transition metal salts and the water soluble Group I–B metal salts, including mixtures thereof, maintaining in the bath during plating a concentration of ammonium hydroxide in excess of 20 grams/liter, calculated as ammonia, up to about the saturation level by feeding ammonia to the bath.

11. The improvement of claim **10** wherein the concentration of ammonium hydroxide maintained in the bath during plating is between 55 and 65 grams/liter, calculated as NH_3 and wherein said member is selected from the group consisting of palladium, cobalt, copper, platinum and rhodium, including mixtures thereof.

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