United States Patent Office

3,032,436
Patented May 1, 1962

3,032,436

METHOD AND COMPOSITION FOR PLATING BY CHEMICAL REDUCTION

Ernest L. Gostin, Boonton, and Stewart D. Swan, Coytesville, N.J., assignors to Metal Processing Co., Inc., Cedar Grove, N.J., a corporation of New Jersey

No Drawing. Filed Nov. 18, 1960, Ser. No. 70,129
9 Claims. (Cl. 117—71)

This invention relates to plating by chemical reduction and more particularly to a method and bath for plating metallic articles and metallic coated articles with a tenacious relatively thick smooth bright gold coating and without the use of electricity by simple immersion of the article in a bath of suitable composition.

Metals have heretofore been plated with gold by several known procedures, including electrolytic plating, immersion in gold salt solutions, and by reduction of gold from gold solutions. Each of these known procedures has certain disadvantages.

Electrolytic processes require careful control of bath compositions, plating current and voltage in order to obtain bright uniform deposits, particularly on irregularly shaped objects and in addition, electrolytic processes require expensive electrical apparatus.

Formulas and methods for using common immersion plates, including gold are described in the Metal Finishing Guide Book, 27th edition (1959), page 469 et seq. These are used when extremely thin plating thicknesses are desired, e.g. those a few millionths of an inch in thickness. In these processes no reducing agents are used and because of the relative nobility of gold as compared with most common metals, articles of copper, copper alloys or zinc may be plated by immersion in a bath containing a gold salt in solution. In the process, the deposition of metals depends entirely on replacement, that is, an exchange occurs in which a slight amount of metal from the surface of the article passes into the solution and an equivalent amount of gold plates out from the plating solution and onto the article. This is a surface reaction and does not proceed after the surface is covered with the metal in solution. Hence the process operates only for a brief interval after which the gold deposited on the surface effectively prevents the base metal from entering the solution, and hence the plating ceases and is extremely thin.

Another procedure which has been employed, particularly in the manufacture of gold mirrors has involved the use of solutions of reducing agents to react with the gold in a gold solution and to deposit elemental gold from the solution. These also are very thin.

Since the work of Brenner and Riddell at the U.S. Bureau of Standards describing the deposition of cobalt and nickel through chemical reduction in a hypophosphite bath, there has been a growing demand for the deposition of gold by a chemical reduction process. Specifically there exists a need for an effective system for the coating of electronic components having intricate or deep-seated configurations, and particularly for an improved process for depositing gold in coating thicknesses exceeding those obtainable by the electroless hypophosphite process taught in Roux Patent 1,207,218. The life of such hypophosphite baths has been found to be limited due primarily to the phosphite and a phosphate build-up and auto-degeneration of the reducing agent.

One object of this invention is to provide a bath which rapidly and uniformly deposits a bright, smooth gold plate on metal articles immersed therein.

A further object is to provide a bath which is simple to operate and which will deposit thicknesses of upwards of 0.001 inch of gold as a plating on metal articles.

Still another object is to provide a bath which will operate satisfactorily when loaded with 0.1 square inch and more of surface area to be plated per gallon of bath.

Still another object is to provide a plating process which eliminates the need for expensive or complicated apparatus and which produces gold plating in which the gold content is at least 99% of the total plated deposit.

These and other objects of the invention will be apparent from the following description and the appended claims.

In general the process comprises: (1) preparing a suitable complexed gold-bearing solution including one or more: buffering agents, additives to adjust the pH of the bath, and reducing agents and (2) maintaining the bath composition and temperature within definite ranges to produce a desirable rate of deposition of a gold plating with desired characteristics. The process is applicable to the plating of gold on both ferrous and non-ferrous metals, but since the coating is most advantageously accomplished on nickel, copper or silver to which metals the gold plating adheres best, it is preferred to provide an intermediate layer of nickel, copper or silver on metallic or non-metallic articles which it is desired to coat with gold. However, gold may be plated directly on iron, steel and other ferrous alloys as well as silver, brass, bronze or other non-ferrous alloys.

As noted above, the plating baths of this invention provide a gold plating on metal articles or metal coated non-metallic articles immersed therein by chemical reduction and do not require any impressed potential as in electrolytic plating.

In the plating baths of this invention, the preferred gold bearing constituent is potassium gold cyanide which is commercially available in sufficient purity for the present processes.

The second essential constituent of our electroless plating bath is a reducing agent for the gold compound dissolved. Although any of a wide variety of reducing agents may be employed, hydrazine hydrate is the reducing agent preferred by us. Other reducing agents which have been used to satisfactorily deposit gold on metal surfaces include other hydrazine derivatives, alkali metal borohydrides, glucose and other sugars, hydroquinones, alkali metal hypophosphites and the like.

The presence of a buffer has also been found to be desirable because deposits obtained from nearly neutral baths appear to be superior to deposits obtained from very acid or very alkaline baths. A preferred buffer in our bath is ammonium citrate, but other alkali metal salts of acetic, citric or other similar carboxylic acids may also be used to this end.

Finally the bath may contain a relatively weak acid or base added to produce the desired pH. Ammonia, ammonium hydroxide, citric acid and other acids and bases have been found suitable.

The following examples are intended to further illustrate this invention and are not to be taken as limitative.

EXAMPLE 1

A plating bath was prepared consisting of the following:

Ingredient:	Concentration (grams per liter)
Potassium gold cyanide	3
Ammonium citrate	90
Hydrazine hydrate	.0002
Water, balance to make 1 liter.	

Ammonium hydroxide was added to adjust the pH.

The amount of gold deposited has been found to vary with changes in temperature, concentration of reducing agent and the pH of the bath.

The compositions of the plating baths of Example 1

indicated below have been operated at temperatures ranging from 70° C. to 100° C.:

Ingredient:	Concentration (grams per liter)
Potassium gold cyanide	0.2–10
Ammonium citrate	10–200
Hydrazine hydrate	0.0001–1
NH_4OH, to give pH between 3 and 12.	

The above baths operated satisfactorily at temperatures from 70° C. up to 100° C. and at pH values ranging from 3 to 12. Optimum gold plating was obtained at pHs from 7 to 7.5 and the preferred bath temperature range was found to be from 92° C. to 95° C.

EXAMPLES 2–4

Three other specific formulations which plated gold on metal substrates in accordance with this invention had the following formulations:

	Grams per liter
Potassium gold cyanide	5
Ammonium citrate	80
Hydrazine	.0001
Potassium gold cyanide	3
Ammonium citrate	90
Hydroquinone	.001
Potassium gold cyanide	3
Ammonium citrate	90
Sodium hypophosphite	8

The formulation described in Example 1 produced the best-appearing gold and was much more stable over longer periods of time than those in Examples 2–4.

The gold deposition was continuous as evidenced by an increase in the weight of gold deposited on test panels left in the specific bath of Example 1 for longer intervals as may be seen from the data in Table 1:

Table 1

Temperature, ° C.	No. of Panels	Thickness deposited (inches)			
		1st Hour	2nd Hour	3rd Hour	Total
92–93	5	0.000051	0.000050	.000053	0.000154
93–92	5	0.000060	0.000040	.000053	0.000153
93	5	0.000075			0.000075
93–94	5	0.000144	.000139		0.000282
94–93	5	0.000145	.000111		0.000256
95	5	0.000287			0.000287

Deposits having considerable thicknesses of about 0.001 inch of gold have been obtained by leaving the articles in the bath for a sufficient length of time as shown by the following data in Table 2:

Table 2

Panel A (92–94° C.)		Panel B (92–95° C.)	
Time (hrs.)	Total Thickness (in.)	Time (hrs.)	Total Thickness (in.)
6	0.0002	5	0.0005
12	0.0006	10	0.0007
16	0.0008	15	0.0009
20	0.001		

From time to time, and preferably continuously, the bath should be replenished by addition of reducing agent and pH adjusting material in small amounts. For continued operation, a gold bearing material must also be added to maintain the gold concentration in the range indicated and to thereby maintain the bath effectiveness.

Each of the above described baths has been successfully employed to deposit gold on resistors and other electronic components, of metal or of ceramic, plastic or other non-metallic materials, coated with an intermediate metallic layer.

In accordance with the patent statutes we have described the invention and the best method of practicing the same. The above description is intended to be illustrative and we do not desire to be limited to the order of steps of such process as herein recited, or to the specific proportions of such parts employed therein, or to the precise ingredients named therein, as it is evident that each of these ingredients has a considerable range of equivalents, and as it is also evident that the order and proportions of the process may be carried out without departing from its scope and purposes.

What is claimed as new is as follows:

1. A method of gold plating metallic surfaces which consists in immersing an article having a metallic surface in a bath containing from 0.2 to 10 grams per liter of potassium gold cyanide, from 10 to 200 grams per liter of ammonium citrate, and from 0.0001 to 1.0 gram per liter of hydrazine hydrate; and in further adding a small quantity of pH adjusting substance, sufficient to adjust the pH of the bath to a desired value between 3 and 12 and in adding constantly to the bath a solution of hydrazine hydrate, and small quantities of the potassium gold cyanide to replenish the gold content of the bath and in maintaining the bath at a temperature between 70° C. and 100° C.

2. The method of gold plating metallic surfaces as claimed in claim 1, wherein the article to be gold plated is first coated with a coating of a metal selected from the group consisting of copper, silver and nickel, before being immersed into the bath.

3. The method of gold plating metallic surfaces which consists in immersing an article consisting of metallic constituents selected from the group consisting of iron, steel, silver, copper, brass, bronze and nickel in a bath containing from .2 to 10 grams per liter potassium gold cyanide, from 10 to 200 grams per liter ammonium citrate, and from 0.0001 to 1.0 gram per liter hydrazine hydrate; and in adding to the bath a gold replenisher solution of potassium gold cyanide and ammonium citrate sufficient to maintain the gold content of the bath and a solution of hydrazine hydrate sufficient to continue deposition of the gold, while maintaining the pH of the bath between 3 and 12 and the temperature of the bath between 70° C. and 100° C.

4. A method of gold plating metallic surfaces which consists in immersing an article consisting of metallic constituents selected from the group consisting of iron, steel, silver, copper, brass, bronze and nickel in a bath containing from 0.2 to 10 grams per liter potassium gold cyanide, from 10 to 200 grams per liter ammonium citrate, and from 0.0001 to 1.0 gram per liter hydrazine hydrate; and in adding ammonium hydroxide to adjust the pH of the bath to a value of between 3–12 while maintaining the bath at a temperature of between 70–100° C. and in replenishing constantly the bath forming chemicals and the pH adjusting ammonium hydroxide to maintain the pH at a constant value.

5. The method of gold plating metallic surfaces which consists in immersing an article having a metallic surface in a bath containing 3 grams per liter potassium gold cyanide, 90 grams per liter ammonium citrate, and 0.0002 gram per liter hydrazine hydrate, maintaining the bath at a temperature of approximately 92° to 94° C. and at a pH of between 7–7.5.

6. A method of gold plating metallic surfaces which consists in immersing an article having a metallic surface in an aqueous bath containing from 0.2 to 10 grams per liter of potassium gold cyanide, a buffer consisting of an alkali metal salt of an aliphatic carboxylic acid and a pH adjusting substance in sufficient amount to provide a pH in the bath of between 3 and 12, and from 0.001 to 1.0 gram per liter of hydrazine hydrate reducing agent, and in maintaining the metallic surface to be gold plated in the bath while the bath is maintained at a temperature between 70° C. and 100° C.

7. A plating bath for depositing gold on a metallic substrate wherein the bath comprises:

0.2 to 10 grams per liter of potassium gold cyanide
10 to 200 grams per liter of ammonium citrate
0.0001 to 1 grams per liter of hydrazine hydrate
balance water.

8. The plating bath of claim 7 wherein the proportions are:

3 grams per liter potassium gold cyanide
90 grams per liter ammonium citrate and
0.0002 grams per liter hydrazine hydrate.

9. The bath of claim 7 including in addition ammonium hydroxide in an amount sufficient to provide a pH between 3 and 12.

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