Patented Nov. 24, 1953

2,660,554

UNITED STATES PATENT OFFICE

2,660,554

BRIGHT GOLD AND GOLD ALLOY PLATING BATHS

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No Drawing. Application November 10, 1950, Serial No. 195,139

5 Claims. (Cl. 204—43)

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The present invention is directed to electrolytic baths, more particularly to baths for the deposition of gold and alloys containing gold.

It has been customary for many years in the plating of gold to utilize a bath consisting essentially of gold cyanide together with other substances. If alloys of gold were to be deposited, the bath contained soluble salts of other metals, such as copper. It has been found that in the electrolytic deposition of gold for the purpose of plating various objects, a smooth gold deposit was difficult to obtain in a single operation. It was also difficult to deposit relatively heavy gold plate so that it was ductile and smooth. In order to overcome these disadvantages, it was proposed to deposit gold on a suitable basis metal in a relatively thin plate and then treat the deposit by a suitable heating cycle and then polishing, buffing or burnishing the deposit. Such a finishing operation was necessary since the deposit was dull and lacked the necessary smoothness, even to the point of being rough.

When heavy deposits were desired, it was necessary to repeat the cycle two or three times, or in other words, the first deposit was heat treated and buffed, after which a second and a third deposit was made with intermediate and final heat treatment and polishing operations. Such procedure was quite costly in that the article being plated was handled a number of times in various operations. Also, the polishing operation removed gold so that the plate became thin and particularly the removal of the gold deposit was considerable where sharp corners and edges were present. It is at such points that the maximum protection is desired and as a result the protection was not sufficient to prevent corrosion of the article over extended periods.

In another procedure it had been proposed to provide a bath containing a gold cyanide in a relatively strongly alkaline solution with the addition of glue. Such an addition was intended to give a bright deposit but it was only moderately successful in that a truly bright finish was not obtained. Glue concentrations are critical and the presence thereof caused deposits to become brittle so that flaking of the deposit often occurred with increasing concentrations of glue. Polarization at the cathode during the operation was increased, introducing difficulties in the operation of the bath.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in prior methods of the type described. it being among the objects of the present invention to provide an electrolytic bath for the deposition of gold and alloys thereof whereby in a

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single operation smooth and heavy gold deposits may be obtained.

It is also among the objects of the present invention to provide an electrolytic bath for the deposition of gold alloys thereof, in which the deposits are bright or semi-bright.

It is further among the objects of the present invention to provide a bath composition which will not interfere with the electro-deposition or the operation of the process and which will accomplish the desired results.

It is still further among the objects of the present invention to provide a bath of the character described which will deposit gold and its alloys in such a state that no finishing operations are necessary thereon and particularly avoiding the necessity for burnishing or buffing the surface of the deposit.

In practicing the present invention there is provided a bath of the usual character containing gold cyanide, usually with other substances such as are commonly used in the art. There is added thereto an organic compound having special properties and particularly imparting to the bath the ability to deposit gold or gold alloys with a bright finish or a semi-bright finish. The degree of brightness may be readily controlled by altering the conditions of deposition. The brightness of the deposits obtained by the present invention are equivalent to the degrees of brightness in the deposition of bright nickel deposits by present day methods. The deposits of the present invention have a much greater resistance to corrosion than equivalent thicknesses of gold or alloys thereof deposited by prior art methods.

The substance added to the bath is one taken from the class of substituted ammonias. At least one of the hydrogen atoms of the ammonia is replaced by an organic radical having from 1 to 12 carbon atoms. The organic radical may be merely a hydrocarbon group or the group may have certain substituent radicals thereon. For instance, at least one of the hydrogens of the organic radical may be replaced by an amino group or an OH group. While ordinarily the organic radical is of the aliphatic type, aromatic radicals may be used. The following are typical of the character of compounds used in the present invention:

Ethylene diamine
Diethylene triamine
Triethylenetetramine
Tetraethylenepentamine
Hydroxyethyl ethylene diamine
Aminoethylethanolamine

The following compounds have also been found suitable for the purpose:

Monoethanolamine
Triethanolamine
Triisopropanolamine

With these compounds the best results are obtained if they are mixed with substances of the first listed group.

Not only the above mentioned substances may be used but others falling within the general class are adapted to give the desired results. It is desirable that the amount of alkali metal cyanide present in the bath be within a definite range depending on the quantity of and the particular alloying metals in the bath (other than gold). In this connection there is used the term "theoretical free cyanide." This term is defined as the quantity of alkali metal cyanide above or less than the amount theoretically necessary to form complex cyanide ions with all of the metals present in the bath. It represents that portion of the alkali metal cyanide which in theory is not combined with the metals present to form the complex salts. The amount of the theoretical free cyanide in the bath varies with the specific amine used, with the operating temperature, and the concentration of metal salts in the solution and may be either positive or negative. It may be desirable to age a fresh bath in order to establish an equilibrium between the various ions in the bath so as to obtain uniform results during the electroplating. The time necessary for aging varies with the temperature and with the particular salts of the alloying metals used in the makeup of the bath; usually, the bath is allowed to stand at room temperature for twenty-four hours. For good adhesion to basis metal, it is desirable to "strike" in a conventional gold cyanide solution prior to plating in these solutions.

Example 1

The following is an example of a bath made in accordance with the present invention:

Gold metal	1.5 gms. per liter added as gold cyanide (AuCN).
Copper metal	1.0 gm. per liter added as copper sulphate.
Nickel metal	4.0 gms. per liter added as nickel sulphate.
Ethylenediamine	35.0 gms. per liter.
Theoretical free KCN	+2.0 gms. per liter.
Water to make 1 liter.	
H_2SO_4 to pH=10.5.	

The temperature of operation is preferably at 140° F. with a current density of from 5 to 100 amperes per square foot. The pH of the solution is between 8.0 and 11.5. As a result of the plating, a single operation gives a deposit which is highly adherent and has a high degree of brightness.

Example 2

The following bath composition has been found suitable for the present purpose:

Gold metal	3.0 gms per liter added as gold cyanide.
Copper metal	2.0 gms. per liter added as copper sulfate.
Nickel metal	8.0 gms. per liter added as nickel sulfate.
Silver metal	0.75 gm. per liter added as silver nitrate.
Diethylenetriamine	35.0 gms. per liter.
Theoretical free KCN	+1.5 gms. per liter.
Water to make 1 liter.	
H_2SO_4 to pH=10.5.	

The conditions of the operation are approximately the same as those set forth in Example 1. The deposit has the desirable characteristics noted above and the deposition may be continued to give as heavy a plate as desired. The surface of the finished article is smooth and quite bright and does not require any finishing operations. The protection against corrosion is excellent.

Example 3

Gold (metal)	4.5 gms. per liter added as gold cyanide.
Nickel (metal)	12.0 gms. per liter added as nickel sulphate.
Copper (metal)	3.0 gms. per liter added as copper sulphate.
Theoretical free KCN	—2.0 gms. per liter.
Aminoethylethanolamine	30.0 gms per liter.
Tetraethylenepentamine	10.0 gms. per liter.
H_2SO_4 to pH=9.5.	

The deposition of the metals takes place under the usual conditions and the temperature may vary from room temperature to about 180° F.

Example 4

Gold (metal)	4.5 gms. per liter added as gold cyanide.
Nickel (metal)	0.5 gms. per liter added as nickel sulphate.
Theoretical free KCN	+2.0 gms. per liter.
Triethylenetetramine	35.0 gms. per liter.

Although the invention has been described setting forth several specific embodiments of the invention, such examples are intended to illustrate the wide variety of compositions which may be used. Any of the usual gold plating baths may have the amino compound incorporated therein with good results. Not only single amino compounds are applicable, but also mixtures which are in many cases particularly effective. The metal or metals to be deposited may be introduced into the bath composition as the amino derivatives, at least in part, and they serve a double function. The conditions of operation include a pH of 3.0 to 11.5 with an optimum of about 9.5 but the invention will still be operative if these limits are exceeded somewhat.

The amount of amino compound used may be varied and good results have been obtained with from 1 to 100 gms. per liter. Instead of inorganic salts of the metals to be plated, organic compounds may in some cases be used in whole or in part. For instance, copper salts of ethylenediamine may replace copper sulphate. The following are compounds of this character:

$CuEn_2.H_2O(Cu(CN)_2)_2$
$CuEn_2(Cu_2(CN)_3)_2$
$CuEn_2Cu_3.2H_2O$
$Cu_2En_2.H_2O(Cu(CN)_3)_2$

wherein En represents ethylenediamine. In the operation of a bath containing copper compounds, gradual reduction to cuprous compounds may occur to such an extent as to interfere in some measure with the brightness of the plate; to avoid this air may be bubbled through the bath at intervals to reoxidize the copper to the cupric form. Or, hydrogen peroxide may be added for this purpose. Alloying metals may be added in the form of compounds which are soluble in the solution, such as metal cyanides, sulphates or chlorides. If, for instance, cuprous cyanide is used, it is preferably oxidized to the cupric state with suitable oxidizing agents.

These and other changes may be made in the details of the invention without departing from the principles herein set forth, and the invention is to be broadly construed and to be limited only by the character of the claims appended hereto.

I claim:

1. An electrolytic bath for plating a metallic material selected from the group consisting of gold and gold-base alloys comprising an aqueous

solution of aurous cyanide having therein a sufficient amount of an amine taken from the class consisting of alkylene- and alkylol-amines having 1 to 12 carbon atoms to produce a brighter deposit than is obtained by plating from said bath in the absence of said substance, and containing about 1.5 to 2.0 grams of theoretical free alkali metal cyanide, the pH being from about 8.0 to about 11.5, whereby heavy gold deposits which do not require burnishing are obtainable by electrolytic deposition.

2. An electrolytic bath for plating a metallic material selected from the group consisting of gold and gold-base alloys comprising an aqueous solution of aurous cyanide and a soluble salt of at least one other metal having therein a sufficient amount of an amine taken from the class consisting of alkylene- and alkylol-amines having 1 to 12 carbon atoms to produce a brighter deposit than is obtained by plating from said bath in the absence of said substance, and containing about 1.5 to 2.0 grams of theoretical free alkali metal cyanide, the pH being from about 8.0 to about 11.5, whereby heavy gold deposits which do not require burnishing are obtainable by electrolytic deposition.

3. An electrolytic bath for plating a metallic material selected from the group consisting of gold and gold-base alloys comprising an aqueous solution of aurous cyanide having therein a sufficient amount of an alkylene amine in which the alkylene radical contains 1 to 4 carbon atoms to produce a brighter deposit than is obtained by plating from said bath in the absence of said substance, and containing about 1.5 to 2.0 grams of theoretical free alkali metal cyanide, the pH being from about 8.0 to about 11.5, whereby heavy gold deposits which do not require burnishing are obtainable by electrolytic deposition.

4. An electrolytic bath for plating a metallic material selected from the group consisting of gold and gold-base alloys comprising an aqueous

solution of aurous cyanide having therein a sufficient amount of an alkylol amine in which the alkylol radical contains 1 to 4 carbon atoms to produce a brighter deposit than is obtained by plating from said bath in the absence of said substance, and containing about 1.5 to 2.0 grams of theoretical free alkali metal cyanide, the pH being from about 8.0 to about 11.5, whereby heavy gold deposits which do not require burnishing are obtainable by electrolytic deposition.

5. An electrolytic bath for plating a metallic material selected from the group consisting of gold and gold-base alloys comprising an aqueous solution of aurous cyanide having therein a sufficient amount of an amine taken from the class consisting of alkylene- and alkylol-amines having 1 to 12 carbon atoms to produce a brighter deposit than is obtained by plating from said bath in the absence of said substance, said amount being from 1 to 100 grams per liter, and containing about 1.5 to 2.0 grams of theoretical free alkali metal cyanide, the pH being from about 8.0 to about 11.5, whereby heavy gold deposits which do not require burnishing are obtainable by electrolytic deposition.

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