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BRIGHT METAL PLATING

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The present invention relates to an improved method and bath for bright electroplating metals and particularly for the bright plating of the noble metals, gold and silver and their alloys.

Various types of baths containing brighteners are already known for the bright electroplating of metals. A large number of organic and inorganic materials have been used as brighteners, but such brighteners are often only effective for the bright plating of a single metal or do not permit continued use in view of their low stability. It has been proposed to employ carbon disulfide as a brightener in silver electroplating baths, but the low solubility of carbon disulfide in the plating baths causes difficulties and must therefore be employed in emulsified form. Another sulfur containing brightener which has been proposed, for example, is a xanthate which does not exhibit the difficulties caused by the low solubility of carbon disulfide. The brightening effect obtained with such sulfur containing brighteners evidently depends upon sulfur being built in to a certain extent in the silver being deposited and the optimum brightening effect evidently depends upon having an exactly predetermined amount of sulfur taken up by the silver deposit. The problem, in producing bright electroplating baths for plating noble metals, therefore, essentially lies in finding sulfur compounds whose controlled decomposition under the conditions of the electrolysis cause the optimum quantity of sulfur to be taken up by the deposited noble metal. However, it must be taken into consideration, that too heavy a liberation of sulfur with formation of metal sulfides easily leads to the production of spongy deposits which not only lead to undesirably high consumption of the brightener but also to a loss of noble metals and cause a deterimental decrease in the brightening effect obtained.

In accordance with the invention, it was found that condensation products of carbon disulfide and acrolein or α substituted acrolein, such as, α methyl acrolein such as produced in alkaline media, act as good brighteners in bright plating of noble metals. These condensation products have the advantage that they are soluble in alkaline plating baths and practically do not decompose in such a way as to contaminate the baths even after long use of the baths containing them. It was unexpectedly found that the brightening effect of such condensation products is not only substantially better than those of carbon disulfide and xanthate but also that they are suited for gold plating baths as well as for silver plating baths. The latter is most surprising as none of the previously employed brighteners could be effectively employed in plating both metals.

The condensation product which is used as a brightener in electroplating baths according to the invention, for example, can be produced as follows: 1600 grams of carbon disulfide are mixed with a solution of 850 grams of NaOH in 4 liters of water and then adding 1200 grams of acrolein with stirring while maintaining the temperature as much below 20° C. as possible. After the reaction mixture has cooled it is poured into acidified water and boiled. The condensation product produced as already indicated is easily soluble in alkalies.

Instead of starting with carbon disulfide, it is also posisible to start with xanthate which is more easy to handle. For example, 1 kilogram of potassium ethyl xanthate can be suspended in 500 cc. of water and 400 cc. of acrolein are added to the suspension with strong stirring. After short heating to about 100° C., the condensation product can be precipitated with water or a 0.5% aqueous acetic acid solution. In the first instance a pH of 10.11 is obtained and in the latter instance a pH of 6–7 is obtained. The condensation product is carefully dried at as low a temperature as possible.

To obtain the best brightening effects it is of certain significance to maintain the concentration of the condensation product according to the invention within a certain range. It was found that good effects could be obtained with baths containing 0.2 to 1.5 grams of the condensation product per liter, and that especially good results can be obtained with concentrations of 0.4 to 1.0 gram per liter.

It is possible to improve the effectiveness of the brightener according to the invention and above all its stability during continued use by the addition of relatively small quantities of water soluble polyglycol esters of fatty acids to the baths. Preferably such esters are those obtained from fatty acids containing 4–15 carbon atoms and about 20 mols of ethylene oxide. The quantity of such polyglycol esters incorporated in the baths according to the invention can, for example, be 0.1 to 2 grams and preferably 0.2 to 0.8 gram per liter of bath liquid.

Optimum brightening effects can be achieved with baths according to the invention which also contain an anionic surface active agent. Sulfonated oils, such as, Turkey-red oil, have been found particularly well suited as such anionic surface active agent. However, all anionic surface active agents are fundamentally suited for this purpose so that instead of or in addition to Turkey-red oil, other sulfonated oils, soaps, fatty alcohol sulfonates, condensation products of fatty acids with oxy- or aminosulfonic acids or albumin decomposition products and high molecular weight alkyl and alkyl aryl sulfonates can come into consideration. Generally the anionic surface active agents can be used in quantities of 0.2 to 4.0 grams per liter and preferably 0.5 to 2.0 grams per liter of bath liquid.

As has already been indicated, the brightener according to the invention is not only effective in producing bright silver platings but also bright gold and bright gold-silver alloy platings. It was found however that it is advantageous in the case of gold and gold-silver alloy electroplating baths to use baths containing a high content of free cyanide. The gold to cyanide ratio preferably should be between about 1:20 to 1:60. Conductive salts such as carbonates or phosphates can also be incorporated in the gold plating baths.

The brightening effect of the baths according to the invention is independent of the thickness of the plating produced in wide ranges, so that generally platings of any desired thickness between several μ and 100 μ and more can be produced with equally good results. It is of course essential that the plating bath is free of dirt. In using the new bath according to the invention one must take into consideration that in some instances a weak brown colored film forms on the anode when the bath stands with the current cut off, and such film upon switching on of the current again can lead to an abnormal increase in potential. This phenomena is often accompanied with the formation of a light haze on the cathode. This haze however can easily be removed without difficulty by polishing. The formation of the film on the anode and haze on the cathode however can easily be avoided by adding a small amount of fresh brightener to the baths at the beginning of the passage of current. The increase in potential and haze formation on the cathode are thereby avoided with certainty.

The brightening effect according to the invention can also be promoted by moderate movement of the plating bath. For this purpose, in general, a simple quiet movement of the cathode suffices. On the other hand, turbulent currents are in any event to be avoided in the plating baths.

The following examples will serve to illustrate several modifications according to the invention:

Example 1

An aqueous bath for bright plating of silver of the following composition was prepared:

	Grams per liter
Ag in form of $KAg(CN)_2$	30
KCN	70
K_2CO_3	40
Carbon disulfide-acrolein condensation product according to invention	0.75
Polyglycol ester of 20 mols ethylene oxide and a mixture of fatty acids containing 4–9 carbon atoms	0.5
Turkey-red oil	1

When this bath was used to silver plate a precleaned copper base at 70° C., at a currrent density of 2 amp./dm.^{2} and a voltage of 0.4 volt with moderate movement of the cathode, silver platings of high brightness were obtained.

Example 2

An aqueous bath for bright plating gold of the following composition was prepared:

	Grams per liter
Au as $KAu(CN)_2$	8
KCN	130
K_2HPO_4	40
Carbon disulfide-acrolein condensation product according to the invention	0.9
Polyglycol ester as in Example 1	0.6
Turkey-red oil	1.2

When this bath was employed at a temperature between 20 and 50° C., current densities between 0.5 and 2 amp./dm.^{2} and a voltage of 0.4 volt, brilliant gold platings up to 20 μ and more thick were obtained.

Example 3

An aqueous bath for bright plating a gold and silver alloy containing 73 to 76% of the following composition was prepared:

	Grams per liter
Au as $KAu(CN)_2$	4
Ag as $KAg(CN)_2$	0.4
K_2CO_3	20
KCN	80
Carbon disulfide-acrolein condensation product according to the invention	0.4
Polyglycol ester as in Example 1	0.3
Turkey-red oil	0.6

Good bright Au-Ag alloy platings were obtained with this bath at 40° C. with current densities between 1 and 1.4 amp./dm.^{2}.

The baths according to the invention furthermore have the advantage that the platings obtained are relatively harder than those obtainable with previously known electroplating baths. For example, whereas galvanically produced pure gold platings normally have a hardness of about 65 kg./mm.^{2}, the platings obtained with the bath of Example 2 had a hardness of 110–130 kg./mm.^{2}. The hardness of the plating obtained with the bath according to Example 1 was also 110–130 kg./mm.^{2} and the hardness of the plating with the bath according to Example 3 was even higher, namely, 140–160 kg./mm.^{2}.

We claim:

1. A bright metal electroplating bath for electroplating a metal from the group consisting of gold, silver and gold-silver alloys comprising an aqueous cyanide solution of a salt of the selected metal and containing as a brightener a condensation product of carbon disulfide and an unsaturated aldehyde selected from the group consisting of acrolein and its alpha substitution products products in an amount sufficient to impart brightness to the electro-deposited metal.

2. A bright metal electroplating bath for electroplating a metal from the group consisting of gold, silver and gold-silver alloys comprising an aqueous cyanide solution of a salt of the selected metal and containing as a brightener a condensation product obtained by condensing an alkali metal xanthate with an unsaturated aldehyde selected from the group consisting of acrolein and its alpha substitution products in an amount sufficient to impart brightness to the electro-deposited metal.

3. A bright metal electroplating bath according to claim 1 in which the quantity of said condensation product is 0.2 to 1.5 grams of the condensation product per liter of bath.

4. A bright metal electroplating bath according to claim 1 in which the quantity of said condensation product is 0.4 to 1.0 gram of the condensation product per liter of bath.

5. A bright metal electroplating bath according to claim 1 comprising in addition 0.1 to 2.0 grams per liter of bath of a water soluble polyglycol ester of a fatty acid containing 4 to 15 carbon atoms.

6. A bright metal electroplating bath according to claim 1 comprising in addition 0.2 to 0.8 gram per liter of bath of a water soluble polyglycol ester of a fatty acid containing 4 to 15 carbon atoms.

7. A bright metal electroplating bath according to claim 1 comprising in addition 0.2 to 0.4 gram per liter of bath of an anionic surface active agent.

8. A bright metal electroplating bath according to claim 7 in which said anionic surface active agent is Turkey-red oil.

9. A bright metal electroplating bath according to claim 1 comprising in addition 0.5 to 2.0 grams per liter of bath of Turkey-red oil.

10. A bright metal electroplating bath for electroplating gold comprising an aqueous solution of a gold salt and an alkali metal cyanide and as a brightener a condensation product of an unsaturated aldehyde selected from the group consisting of acrolein and its alpha substitution products and a compound with a >C=S group selected from the group consisting of carbon disulfide and alkali metal xanthate in an amount sufficient to impart brightness to the electro-deposited metal, the ratio of gold to alkali metal cyanide in said bath being between 1:20 and 1:60.

11. A bright metal electroplating bath for electroplating gold-silver alloys comprising an aqueous solution of gold and silver salts and an alkali metal cyanide and is a brightener a condensation product of an unsaturated aldehyde selected from the group consisting of acrolein and its alpha substitution products and a compound with a group >C=S selected from the group consisting of carbon disulfide and alkali metal xanthate in an amount sufficient to impart brightness to the electro-deposited metal, the ratio of gold-silver alloys to alkali metal cyanide in said bath being between 1:20 and 1:60.

12. A method of electroplating a metal selected from the group consisting of gold, silver and gold-silver alloys on a base member which comprises electroplating the

base member in an electroplating bath comprising an aqueous cyanide solution of a salt of the selected metal and containing as a brightener a condensation product of an unsaturated aldehyde selected from the group consisting of acrolein and its alpha substitution products and a compound with a group >C=S selected from the group consisting of carbon disulfide and alkali metal xanthate in an amount sufficient to impart brightness to the electro-deposited metal.

References Cited in the file of this patent

UNITED STATES PATENTS

2,666,738	Kardos	Jan. 19, 1954