

The invention relates to a galvanic gold alloy plating bath which exhibits from 1 to 15 g/l gold as potassium gold(I) cyanide, from 5 to 50 g/l copper as potassium copper(I) cyanide, from 0.05 to 5 g/l silver as potassium silver(I) cyanide, free alkali metal cyanide, dipotassium hydrogen phosphate and a selenium compound, and a pH of from 8.5 to 11.

Galvanic deposition of gold alloys has become particularly important for decorative and technical purposes. The soft, cell-yellow, matt pure gold films are amenable to a wide range of attribute modifications, in terms of for example brightness, hardness, resistance to wear, or colour, which are achieved by co-depositing other metals. 14 to 18 carat yellow or rose-coloured coatings account for a substantial proportion of the gold alloy coatings deposited, and contain in addition to copper as alloying metal a white-coloured metal such as cadmium, silver or zinc, in order to lighten the red tone imparted by the copper.

Such coatings have applications, for example, in the jewellery and spectacle industry, where rolled gold films have to a large extent been replaced by galvanic coatings. Such coatings are, however, also employed in electronics when there is no requirement for low contact resistance, for example in slip ring and rotary contacts.

Galvanic deposition of gold/copper/silver alloy coatings causes considerable problems because of the potential position of the metals in the electrolyte, and as yet there is no satisfactory answer to this. Simultaneous deposition is based on aqueous solutions of the cyano complexes of the three metals. In the alkaline range, the only range in which the said baths are stable, the potential of the silver is substantially more noble than that of gold and copper, thus causing preferential deposition of silver, with the result

that only coatings which are whitish-yellow or greenish-yellow are obtained, depending on the silver content.

DE-PS 801 312 therefore seeks to displace the potential of the silver to less noble values by employing a pH which is as low as possible. However, at a pH 7 such as is indicated, the free alkali metal cyanide which is necessary for stabilising the cyano complexes of the three metals is no longer stable, the concentration constantly fluctuates, thus also causing constant fluctuation in the composition of the deposited alloy. DD-PS 59022 also works in the neutral range and seeks to obtain bright films by applying current alternation at low free alkali metal cyanide concentration, which in practice frequently results in coatings which are not of uniform colour.

Brightness can also be imparted to the coatings in alkaline baths by means of chemical compounds. In accordance with DE-PS 750 185 selenium compounds or tellurium compounds have the effect of imparting brightness when silver or copper coatings are deposited from an alkali metal cyanidic bath.

JP-A-59 76891 (Chem. Abstr., Vol. 101, No. 12, p. 587, 100245f) describes a galvanic gold-silver-copper bath which contains gold, silver and copper as alkali metal cyanides, free cyanide in quantities of less than 10 g/l and hydrogen carbonate, but no selenium compounds. Bright films are obtained only if two gold alloy films of different composition are deposited in superimposed manner at different current densities, and thermal diffusion of the two films into one another is effected at 600°C.

FR-A-22 02 954 discloses a galvanic gold-copper-cadmium bath which contains the alloying metals as alkali metal cyanides, free alkali metal cyanide and a selenium compound in quantities of from 0.1 mg/l to 5 g/l, calculated as selenium,

as brightening agent. This specification contains no reference to galvanic gold-silver-copper baths.

US-A-4,121,982 describes a galvanic gold-silver bath which contains as brightening agent a combination of from 0.1 to 0.5 mg/l of selenium compound and from 4 to 75 mg/l of a polyethylene imine per gramme of silver content or gold content of the bath. Here too there is no reference to galvanic gold-silver-copper baths.

The object of the present invention was therefore to develop a galvanic gold alloy plating bath which exhibits from 1 to 15 g/l gold as potassium gold(I) cyanide, from 5 to 50 g/l copper as potassium copper(I) cyanide, from 0.05 to 5 g/l silver as potassium silver(I) cyanide, free alkali metal cyanide, dipotassium hydrogen phosphate and a selenium compound, and a pH of from 8.5 to 11, which is stable and which provides without costly auxiliary substances bright gold-copper-silver alloy coatings which are yellow to rose in colour, depending on copper content and current density.

This object is achieved according to the invention in that the maximum free alkali metal cyanide content is 10 g/l, and from 0.1 to 1 mg/l selenium is contained as potassium selenocyanate.

The bath preferably additionally contains from 0.1 to 5 ml/l of a surfactant from the group comprising nonionic wetting agents of the ethylene oxide addition compound type and of the phosphate esters thereof. Alkyl polyglycol ethers, butyl or nonyl phenol polyglycol ethers and phosphate esters thereof are examples which may be used.

It has surprisingly proved that in the weakly alkaline range at free alkali metal cyanide contents of ≤ 10 g/l in conjunction with the brightening agent potassium

selenocyanate, not only is it possible to co-deposit a sufficient quantity of copper and for the bath to exhibit stable conditions, but the coatings are also bright and ductile.

The galvanic gold alloy plating baths according to the invention are of the following composition:

1	-	15 g/l	gold as $\text{KAu}(\text{CN})_2$
5	-	50 g/l	copper as $\text{K}_2\text{Cu}(\text{CN})_3$
0.05	-	5 g/l	silver as $\text{KAg}(\text{CN})_2$
0.1	-	10 g/l	free alkali metal cyanide
1	-	10 g/l	dipotassium hydrogen phosphate
0.1	-	5 m/l	surfactant
0.1	-	1 mg/l	selenium as KSeCN

A phosphate ester, such as for example nonyl phenol polyglycol ether phosphate ester, is a suitable surfactant which supports formation of brightness. The bath exhibits a pH of between 8.5 and 11 and is preferably operated at a bath temperature of from 60 to 75°C and at current densities of from 0.2 to 2.5 A/dm².

The following bath composition is preferably used for the 14 to 18 carat yellow or rose gold alloy coatings which are those most frequently deposited in practice:

3	-	5 g/l	gold as $\text{KAu}(\text{CN})_2$
20	-	25 g/l	copper as $\text{K}_2\text{Cu}(\text{CN})_3$
0.2	-	0.5 g/l	silver as $\text{KAg}(\text{CN})_2$
2	-	4 g/l	free alkali metal cyanide
2	-	4 g/l	dipotassium hydrogen phosphate
0.1	-	1 ml/l	surfactant
0.1	-	0.5 mg/l	selenium as KSeCN .

The bath is preferably operated at a pH of from 9 to 10 and at a bath temperature of from 60 to 70°C. Bright coatings are obtained in the current density range 0.3 to 1.5 A/dm², the carat fineness of the films decreasing as current density increases. The deposited films are highly ductile and even low-carat coatings exhibit good resistance to corrosion in the copper chloride test.

The following Example is provided to explain the galvanic gold alloy plating bath according to the invention in greater detail:

The following substances are dissolved sequentially in distilled water for the preparation of a one-litre bath: 2 g potassium cyanide, 69.2 g potassium copper(I) cyanide, 7.5 g potassium dicyanoaurate(I), 2 g dipotassium hydrogen phosphate, 0.46 g potassium dicyanoargentate and 0.18 mg potassium selenocyanate. 0.1 ml of the wetting agent nonylphenol polyglycol ether phosphate ester is added at a dilution of 1 : 5 and water is finally added to make up to 1 litre.

The pH is adjusted to 9 with potassium hydroxide. The bath is now heated to 65°C and a prepared, bright nickel plated copper sheet having a surface area of 0.25 dm² is gold plated 2.5 amine at a current density of 0.5 A/dm². A bright coating having a slight rose tone is obtained which exhibits a carat fineness of 17.2.

Claims

1. Galvanic gold alloy plating bath containing from 1 to 15 g/l gold as potassium gold(I) cyanide, from 5 to 50 g/l copper as potassium copper(I) cyanide, from 0.05 to 5 g/l silver as potassium silver(I) cyanide, free alkali metal cyanide, dipotassium hydrogen phosphate and a selenium compound and exhibiting a pH of from 8.5 to 11, characterised in that the maximum free alkali metal cyanide content of the bath is 10 g/l, and in that it contains from 0.1 to 1 mg/l selenium as potassium selenocyanate.
2. Galvanic gold alloy plating bath according to Claim 1, characterised in that it contains additionally from 0.1 to 5 ml/l of a surfactant taken from the group comprising nonionic wetting agents of the ethylene oxide addition compound type and phosphate esters thereof.

