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IODATE-CONTAINING PLATING BATHS

Fred I. Nobel, North Valley Stream, and Barnet D. Ostrow, North Bellmore, N. Y.

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The present invention is directed to electroplating baths, more particularly to the addition to such baths of substances adapted to increase the effectiveness thereof.

In copper and silver cyanide plating it has been common practice to use sulphur containing additional agents, such as soluble thiocyanates and thiosulphates, in high efficiency baths. Such agents tend to break down during the plating operation, particularly at the higher temperatures used, forming alkali sulphides which narrow the bright plating range and promoting roughness of the deposit. Another undesirable effect of said sulphides was the hardness of the deposit and the difficulty of buffing it. Such sulphides may be brought into the bath incidentally as traces of impurities in the cyanides, in the form of potassium or sodium sulphides.

For example, when sodium thiocyanate is used as a brightener in a bath it breaks down at the high temperature, reacting with alkali metal hydroxide forming alkali metal sulphide and cyanide. In a bath having the following composition—

	Oz./gal.
CuCN	8.0
KCN	12.5
KOH	5.0
NaCNS	2.0

and operated at about 175° F., it will give initially a bright current density range of 0 to 60 amperes per square foot. After a relatively short time of operation, and due to breakdown of the thiocyanate, the operable bright plating range is reduced to about 0 to 20 amperes per square foot.

In another type of bright cyanide copper bath compounds of selenium are introduced. These baths are particularly sensitive to the presence of sulphide sulphur. The presence of the traces of sulphides in the cyanides adversely affects the plating characteristics of such baths. The baths may also be accidentally contaminated by sulphur type compounds, resulting in harmful effects on the bright plating range. For instance, in a bath of the composition—

	G./liter
Silver (as KAg cyanide)	30
Free KCN	30
K ₂ CO ₃	30
Selenium (as Na selenite)	5
Na thiosulphate	0.5
Lampon A	1.0

of the prior art, operated at room temperature with cathodic agitation, has a bright plating range of 0 to 30 amperes per square foot. After the bath has been in operation for some time, the breakdown of the thiosulphate has an adverse effect on the deposit in the low current density areas which will become dull, white and smoky. Furthermore, the bright deposit area is narrowed to approximately 20–30 amperes per square foot.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in the

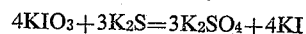
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prior art, it being among the objects of the invention to provide an addition agent to a plating bath which will prevent the disturbing effects of sulphide sulphur.

It is also among the objects of the invention to provide an agent which is intended and adapted to oxidize sulphide sulphur to an innocuous state, such as in the form of sulphate, without affecting the cyanide in silver and copper cyanide plating baths.

It is further among the objects of the invention to introduce an addition agent into acid nickel plating baths in order to secure smoother and better leveled deposits.

In practicing the present invention, there is added to the bath which may be a copper or silver cyanide bath having a pH of at least 7, a small amount of an alkali metal iodate. Preferably it is in the form of the potassium salt. The specific amount used may be varied within wide limits, and the amount is dependent on the amount of sulphide sulphur to be oxidized by the iodate to the sulphate. The reaction is probably as follows:



Usually the amount of the alkali metal iodate which is added to the bath is from .001 to 5.0 g./liter of the aqueous solution. These amounts are usually adequate to take care of the sulphide which is accidentally present or is produced by breakdown of other sulphur compounds. However, in some instances where an unusually large amount of sulphide sulphur is present, larger amounts of the iodate may be necessary. In most cases, considerably less iodate will be sufficient. The sulphate formed is inert and does not affect the operation of the bath.

Other types of oxidizing agents, such as hydrogen peroxide or the like, are incapable of accomplishing the desired results. Such oxidizing agents tend to first oxidize the cyanide in the bath while not acting on the sulphide. Therefore, they are totally unsuitable for the elimination of sulphides.

The following are specific examples of the operation of the invention:

Example 1

A bath of the following composition is used wherein the pH is over 13:

	Oz./gal.
CuCN	8.0
Free KCN	12.5
KOH	5.0
NaCNS	2.0
Cetyl betaine	.25

This bath has a bright plating range at the beginning of the plating of 0 to 60 amperes per square foot. After operation for some time at 170° F. with agitation, the breakdown of the thiocyanate reduces the bright plating range to 0 to 30 amperes per square foot. With the addition of potassium iodate in the amount of .05 to .2 g./liter, the sulphide is oxidized to sulphate and the original bright plating range is restored.

Example 2

The bath has the following composition:

	Oz./gal.
CuCN	8.0
NaCN	9.8
Rochelle salts	6.0
KOH	2.0
K ₂ SeO ₃	.134
Pb tartrate	.013

The contamination in this bath comes mainly from sodium sulphide present in the copper cyanide. The bath is operated at 160° F. with agitation. At the beginning of the operation the bath has a bright plating range of 20–

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to 60 amperes per square foot. Potassium iodate is added in an amount calculated to be sufficient to oxidize the sulphide present, whereby the bright plating range becomes 0 to 60 amperes per square foot.

Example 3

There is provided a bath of a pH of 8.5 having the following constituents:

	G./liter
CuCN -----	60
KCN -----	95
KOH -----	15
Rochelle salts -----	45
Selenourea -----	.004

Plating is conducted at 160° F. with agitation with a bright plating range of 0 to 80 amperes per square foot. As the bath continues to operate the bright plating range is reduced to 0 to 30 amperes per square foot due to the contamination with sulphide. To the bath is added from .002 to 2.0 g./liter, depending on the amount of contamination, of sodium iodate, whereby the original bright plating range is restored.

Example 4

A silver cyanide plating bath of the following composition is provided:

	G./liter
AgCN -----	30
Total KCN -----	50
K ₂ CO ₃ -----	30
KSb tartrate -----	1
K ₂ Se -----	.001

Plating is conducted at 75° F. with agitation at a bright plating range of 0 to 50 amperes per square foot, which drops to 0 to 25 amperes per square foot in a relatively short time. Upon the addition of sufficient potassium iodate to oxidize all of the sulphide sulphur, the original bright plating range is obtained.

Example 5

The silver cyanide bath containing thiosulphate described above wherein after operation the bright plating range has dropped to 20 to 30 amperes per square foot, is treated with an amount of potassium iodate sufficient to oxidize the breakdown products of the thiosulphate. The original bright plating range is restored thereby.

Example 6

It has further been found that the addition of the alkali metal iodate has a beneficial effect in the operation of an acid nickel bath, of which the following composition is typical:

	G./liter
NiSO ₄ ·7H ₂ O -----	300
NiCl ₂ ·7H ₂ O -----	45
H ₃ BO ₃ -----	52.5
Na naphthaline disulphonate -----	15

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The bath is operated at 130° to 140° F. with agitation. In starting with an article having an R. M. S. of 25 μ in., after depositing .001 inch of nickel from the above bath there is no change in the R. M. S. Then there is added to the bath .12 g./liter of potassium iodate and the article is plated under the same conditions, whereby the R. M. S. is reduced to 15 μ in.

In the acid nickel plating baths the concentration of the iodate is usually from .05 to 1.0 g./liter with the optimum range of .10 to .50 g./liter. When concentrations greater than 1.0 g./liter are introduced into the bath, there may be developed some adverse effect on the throwing power of the nickel solution.

We claim:

1. An aqueous metal plating bath comprising an aqueous alkaline solution of a compound taken from the class consisting of copper cyanide and silver cyanide having incorporated therein an amount sufficient to oxidize sulfide sulfur in said bath of an alkali metal iodate.

2. An aqueous alkaline copper cyanide plating bath having incorporated therein an amount sufficient to oxidize sulfide sulfur in said bath of sodium iodate.

3. An aqueous alkaline copper cyanide plating bath having incorporated therein an amount sufficient to oxidize sulfide sulfur in said bath of potassium iodate.

4. An aqueous alkaline copper cyanide plating bath having incorporated therein a small amount of an alkali metal iodate in the amount of .001 to 5.0 g./liter.

5. An aqueous alkaline copper cyanide plating bath having incorporated therein at least .001 gram per liter of an alkali metal iodate.

6. An aqueous alkaline silver cyanide plating bath having incorporated therein at least .001 gram per liter of an alkali metal iodate.

7. An aqueous copper cyanide plating bath containing sulphide sulphur having incorporated therein a sufficient amount of an alkali metal iodate to oxidize said sulphide sulphur.

8. An aqueous silver cyanide plating bath containing sulphide sulphur having incorporated therein a sufficient amount of an alkali metal iodate to oxidize said sulphide sulphur.

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