

Nov. 12, 1957

B. D. OSTROW

2,813,066

ALKYLPOLYAMINE MODIFIED CYANIDE COPPER PLATING BATH

Filed Nov. 14, 1955

2 Sheets-Sheet 1

Fig. I-A



Fig. I-B

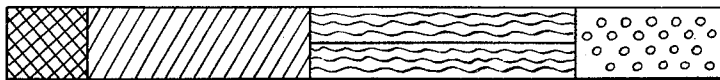


Fig. I-C



Fig. I-D

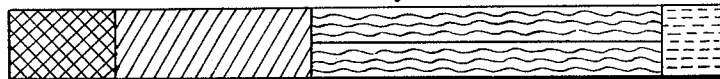


Fig. I-E

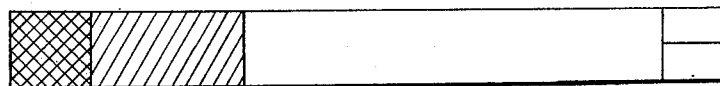


Fig. I-F

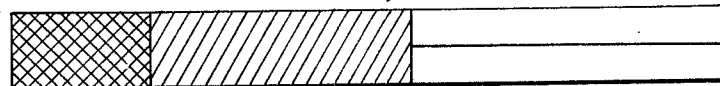
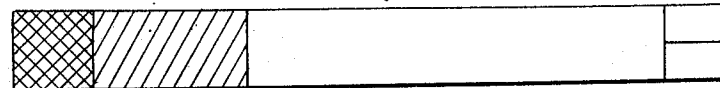


Fig. I-G



INVENTOR.

BARNET D. OSTROW

BY

H. B. Berman

ATTORNEY

Nov. 12, 1957

B. D. OSTROW

2,813,066

ALKYLPOLYAMINE MODIFIED CYANIDE COPPER PLATING BATH

Filed Nov. 14, 1955

2 Sheets-Sheet 2

Fig. II-A

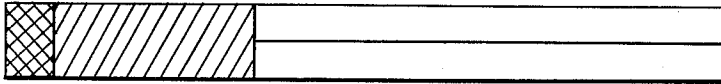


Fig. II-B

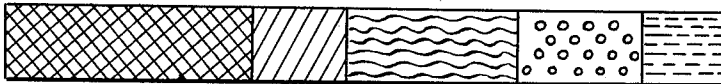


Fig. II-C



Fig. III-A

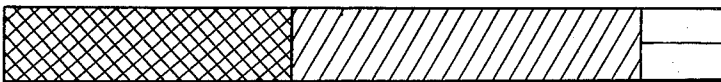
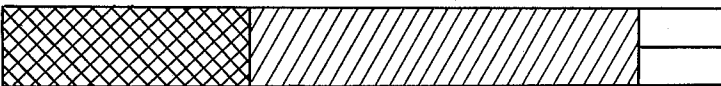


Fig. III-B



Fig. III-C



INVENTOR.

BARNET D. OSTROW

BY

H. B. Berman

ATTORNEY

1

2,813,066

ALKYLPOLYAMINE-MODIFIED CYANIDE
COPPER PLATING BATH

Barnet D. Ostrow, North Bellmore, N. Y.

Application November 14, 1955, Serial No. 546,584

5 Claims. (Cl. 204—52)

The present invention is directed to cyanide copper plating baths, more particularly to an improvement whereby contaminations may be rendered harmless. The present application is a continuation in part of my co-pending application, Serial No. 349,935, filed April 20, 1953, entitled "Electroplating Compositions for Copper," now Patent 2,732,336; and application, Serial No. 479,871, filed January 4, 1955, entitled "Bath for Plating Bright Copper," now abandoned.

Cyanide copper electroplating baths are commonly used in the plating of zinc die castings and of steel for the purpose of depositing a copper plate prior to plating the articles with nickel and chromium. The operation utilizes a plating cycle wherein the same plating racks or fixtures for holding the work pass successively through the copper, nickel and chromium baths. This practice is economical in the sense that it is unnecessary to re-rack the articles between the successive plating baths, but there is the serious disadvantage that there is a tendency to introduce a contamination by soluble salts of nickel or chromium into the copper bath. Particles from zinc die castings often fall into the plating bath and tend to dissolve, thereby introducing soluble zinc salts as an impurity. In particular the high efficiency bright plating baths which are used extensively are particularly affected by such soluble metallic impurities and the low efficiency and Rochelle type baths are equally affected by chromium and zinc contaminants.

It has been proposed to remove soluble zinc impurities by the use of sodium sulfide when the concentration of zinc reached 0.3 oz. per gallon. Such a use has an adverse effect as it tends to lower the bright plating range of said bath by introducing the sulfide ion therein. In such a system when chromium having a valence of +6 enters the cyanide copper bath in concentrations of 15 to 20 parts per million, very harmful side effects are produced, such as loss of efficiency, decrease of covering power and in an extreme case, plating is totally interrupted. The harmful effect of the chromium is accentuated in the presence of zinc salts as impurity.

It has also been proposed to add to the cyanide copper baths sodium hydrosulfite, in order to reduce the chromium to the harmless trivalent form, which then precipitates out. While this is somewhat effective in precipitating chromium, it also introduced into the solution sulfide compounds, such as sodium sulfide, which adversely affected the bright plating range. With zinc present, insoluble zinc sulfides may precipitate and cause roughness of the deposit. It also became necessary to make frequent additions of the hydrosulfite in quantities approximately equal to the concentration of the soluble chromium as an excess of hydrosulfite was harmful.

The present invention is intended and adapted to overcome the difficulties and disadvantages inherent in prior baths of the type described, it being among the objects of the present invention to provide a cyanide copper bath having small amounts of additives therein to increase the tolerance thereof for metallic impurities and particularly in high efficiency bright plating baths.

2

It is also among the objects of the present invention to provide a bath composition wherein such contaminants as zinc, chromium and nickel may be permitted to accumulate to a very substantial degree without detriment to the plating operation.

It is further among the objects of the present invention to introduce into a cyanide copper bath of the usual types, small amounts of additives without impairing the efficiency of the bath and at the same time maintaining the bright plating range thereof.

In practicing the present invention, it has been found that the polyamines in small amounts are very effective in increasing the tolerance of cyanide copper baths to zinc, chromium and nickel and other metals forming soluble complexes. The polyamines have from 2 to 6 amino groups and each of the alkyl groups has from 1 to 3 carbon atoms. While the polyamines as such are preferred, it is also possible to react the polyamines to form condensation products which are also suitable for the purpose.

Baths of this character have excellent tolerance for the above mentioned soluble metallic contaminants. While they are particularly adapted to high efficiency baths, the beneficial effects of such additives are found in practically any cyanide copper bath.

In the accompanying drawing constituting a part hereof and in which like symbols indicate like deposit areas,

Figs. I-A to I-G represent diagrammatically the results obtained in a series of experiments for depositing copper in a standard 267 ml. Hull cell utilizing a standard cyanide copper plating bath;

Figs. II-A to II-C are similar diagrammatical views showing the results obtained utilizing a second standard cyanide copper bath; and

Figs. III-A to III-C are views similar to Fig. I, showing the results obtained using still a third standard cyanide copper bath.

In the drawings, the clear areas represent bright plating on copper strips, and the areas having a single central horizontal line represent semi-bright areas. The cross-hatched areas indicate matte deposits and the doubly cross-hatched areas represent burned deposits. Those areas having a series of horizontal broken lines are areas where no deposit occurred and the areas containing a series of circles indicate deposits which are discolored, being dull and black to grey. Those areas having a series of horizontal wavy lines indicate deposits that are uneven and swirled.

Bath No. I

A standard bath such as has been used in the prior art was utilized in a series of comparative experiments, the bath having the following composition:

	Oz./gal.
Copper cyanide	8.0
Potassium cyanide	12.7
Potassium hydroxide	5.6
Sodium thiocyanate	2.0
Cetyl-betaine	.04

This bath was operated in a No. 267 Hull cell at 175° F. with agitation at 2 amperes for five minutes. As shown in Fig. I-A, it produces a good, bright deposit at current densities from 10 to 40 amperes per square foot.

To this bath there was added potassium chromate in which the chromium has a valence of +6. The amount added was 20 parts per million or .02 grams per liter. The bath was operated as above stated, the results being shown in Fig. I-B. There was a total elimination of the bright areas and there was poor coverage, particularly in the low current density areas.

To this bath containing the potassium chromate, there was added .25 oz. per gallon of tetraethylene pentamine and the bath was operated as before. As will be seen

3

from Fig. I-C, the original characteristics of the bath were restored so that the adverse effect of the chromium was completely eliminated.

To the aforesaid standard cyanide copper bath, there was added 75 parts per million of chromium in the form of potassium chromate. In Fig. I-D, there is shown the results of operation with this bath, the deposits being striated and non-uniform in the high current density areas. There was no deposit in the low current density areas.

To this bath containing the chromium having a valence of +6, there was added .4 oz. per gallon of triethylene tetramine. The bath was operated as before, the results being shown in Fig. I-E. The initial effectiveness of the original bath has been completely restored.

To the aforesaid standard bath, there was added .5 oz. per gallon of zinc in the form of zinc cyanide. Upon operation of the bath, the bright areas were destroyed as shown in Fig. I-F and the deposits were brass to bronze color. To this zinc containing bath, there was added 1.0 oz. per gallon of diethylene triamine. Upon the operation of the bath as before, the brightness of deposit has been restored, as shown in Fig. I-G.

Bath No. II

Another standard bath well-known in the art is as follows:

	Oz./gal.
Copper cyanide.....	6.0
Potassium cyanide.....	9.7
Potassium hydroxide.....	2.0
Potassium carbonate.....	4.0
Rochelle salts.....	6.0

In Fig. II-A is shown the results of a run with this bath at a temperature of 160° F. with agitation for a period of 5 minutes. It indicates a semi-bright deposit up to 50 amperes per square foot. To this bath, there was added 100 parts per million of chromium in the form of potassium chromate. The results of operation of the bath are shown in Fig. II-B. Little or no copper tended to deposit below 20 amperes per square foot and the deposits were discolored, being black to grey. At the higher current densities, the deposits were non-uniform.

To the bath containing the chromium, there was added 1.5 oz. per gallon of triethylene tetramine. Upon the operation of the bath, the harmful effects of the chromium as shown in Fig. II-B were completely nullified. The bath now operated approximately as it had originally before the chromium was added.

Bath No. III

Still another bath commonly used in the art has the following composition:

	Oz./gal.
Copper cyanide.....	4.0
Sodium cyanide.....	6.0
Potassium hydroxide.....	4.0
Sodium carbonate.....	2.0

This bath was operated in a Hull cell for five minutes at a temperature of 140° F. As shown in Fig. III-A, the deposit was smooth, had a matte surface up to 30 amperes per square foot and was burned above this range. Then there was added to the bath, 50 parts per million of chromium in the form of sodium chromate. The results of operation of the modified bath is shown in Fig. III-B. Little or no copper was deposited below 10 amperes per square foot and this had a grey to black tone. At high current densities, the deposit was non-uniform.

To the bath containing the chromium there was added 1.25 oz. per gallon of triethylene tetramine vinyl acetate reaction product. As seen in Fig. III-C, the initial effectiveness of the bath was restored thereby.

Not only the amines themselves but certain reaction products thereof with unsaturated esters, such as vinyl

4

acetate; aldehydes, such as aldol; and acylketones, such as acetonylacetone are effective. Such compounds have from 4 to 10 carbon atoms. In order to prepare such compounds, a mixture is made of a polyamine, vinyl acetate and water, the polyamine being tetraethylene pentamine and the proportions being 10 to 15 to 75 by volume. The reaction is exothermic and the mixture is agitated and warmed in order to cause the reaction to take place. At the end of the reaction, the mixture is heated to boiling for a few minutes. Similarly the reaction products of the other polyamines with the aforesaid compounds may be caused to take place.

In another aspect of the invention, the contamination of a bath with chromium may be reduced by precipitating the chromium compound even in baths containing tartrates or similar radicals. As an example, a polyamine or its reaction product as set forth above is added to the bath. It is then treated with a small amount of an alkaline earth such as calcium or magnesium hydroxides or calcium oxide. This results in a precipitation of the chromium compound having a valence of +6.

In operating this phase of the invention, the Bath No. II, which is contaminated with 100 parts per million of chromium having a valence of +6, is held at a temperature of 140° to 160° F. for about one hour in the presence of 1-2 oz. per gallon of lime. The precipitated material is allowed to settle and is filtered off. About 80% of the chromium present is thus removed. An examination of the filtered precipitate under a spectrograph shows that the chromium has been adsorbed on the alkaline earth by this treatment.

The concentration of the polyamine or its reaction product may vary from .01 to 50 grams per liter. The lower limit used depends upon the concentration of the metallic impurities which are to be nullified. A large excess of the polyamine or its reaction product has no undesirable effect on the plating characteristics of the bath. By this invention, impurities up to 200 to 250 parts per million may be tolerated, whereas 5 or 10 parts per million of such impurities in the standard baths made such baths practically unworkable for plating bright copper.

The polyamines and their reaction products are capable of forming complexes with various bath impurities other than zinc, chromium and nickel, thus sequestering them. Still higher molecular weight polyamines up to a molecular weight of about 2000 are capable of use in accordance with the invention with good results.

What is claimed is:

1. A method of treating cyanide copper plating baths having therein free alkali metal hydroxide and containing soluble contaminants taken from the class consisting of zinc, chromium and nickel which comprises adding to said bath an unsubstituted alkylpolyamine in sufficient amount to sequester said contaminants, said amine having 2 to 6 amino groups and the alkyl groups each having 1 to 3 carbon atoms.

2. A method of treating cyanide copper plating baths having therein free alkali metal hydroxide and containing soluble contaminants taken from the class consisting of zinc, chromium and nickel which comprises adding to said bath an unsubstituted alkylpolyamine in sufficient amount to sequester said contaminants, said amine having 2 to 6 amino groups and the alkyl groups each having 1 to 3 carbon atoms, the concentration of said polyamine being from .01 to 50 grams per liter.

3. A method of treating cyanide copper plating baths having therein free alkali metal hydroxide and containing soluble contaminants taken from the class consisting of zinc, chromium and nickel which comprises adding to said bath an amine selected from the group consisting of unsubstituted alkylpolyamines and alkylpolyamine compounds in sufficient amount to sequester said contaminants, said amine having 2 to 6 amino groups and the alkyl groups each having 1 to 3 carbon atoms, said

5

compound being a reaction product of said alkylpolyamine with a compound taken from the class consisting of unsaturated esters, unsaturated aldehydes and unsaturated acylketones having 4 to 10 carbon atoms.

4. A method of treating cyanide copper plating baths having therein free alkali metal hydroxide and containing soluble contaminants taken from the class consisting of zinc, chromium and nickel which comprises adding to said bath an unsubstituted alkylpolyamine having 2 to 6 amino groups in sufficient amount to sequester said contaminants, said amine having a molecular weight up to about 2000, and the alkyl groups thereof having 1 to 3 carbon atoms.

5. A method of treating cyanide copper baths having therein free alkali metal hydroxide and containing soluble contaminants capable of forming complexes with polyamines which comprises adding to said bath an unsubstituted alkylpolyamine having 2 to 6 amino groups in sufficient amount to sequester said contaminants, said

6

amine having a molecular weight up to about 2000, and the alkyl groups having 1 to 3 carbon atoms.

References Cited in the file of this patent

UNITED STATES PATENTS

2,195,454	Greenspan	Apr. 2, 1940
2,434,191	Benner et al.	Jan. 6, 1948
2,582,233	Chester et al.	Jan. 15, 1952
2,660,554	Ostrow	Nov. 24, 1953
2,662,853	Ellis	Dec. 15, 1953

FOREIGN PATENTS

694,893	Great Britain	July 29, 1953
---------	---------------	---------------

OTHER REFERENCES

Versenes: Bersworth Chem. Co., Framingham, Mass., pp. 46-8, sec. II February 1952.

Gilbertson et al.: Transactions of Electrochem. Soc., vol. 79, pp. 439-442, 1941.