United States Patent Office 2,861,929
Patented Nov. 25, 1958

2,861,929

COPPER PLATING WITH ADDITION AGENTS

Donnan Martin, Niagara Falls, and Arthur H. Parker, Kenmore, N. Y., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application June 20, 1957
Serial No. 667,015

3 Claims. (Cl. 204—52)

This invention relates to improvements in the electrodeposition of copper on base metal and more particularly relates to the production of smooth, bright copper deposits from alkaline cyanide copper plating baths.

In the manufacture of chromium plated parts especially for the automotive industry it is desirable to have a smooth, mirror-like finish. The undercoat of copper below the chromium or nickel tends to deposit on the base metal in such a way as often to exaggerate the surface imperfections, particularly scratch-like and other imperfections, which then prevent the formation of the desired smooth final plate without a costly buffing process applied to the copper plate.

Periodic reversal of the electroplating current (PR) as disclosed by the Jernstedt Patent 2,451,341 is of great assistance in smoothing out the copper plate applied to the base metal but the process is deficient in that relatively poor brightness of the copper plate results and the speed of plating is too slow for present day requirements.

According to the Wernlund Patent 2,701,234 a considerable improvement in the PR plating process results from the combined use of water soluble selenate or selenites with a soluble salt of methylene-bis α-naphthalene sulfonic acid. The bath containing the selenates or selenites together with the sulfonic acid agent has good leveling properties but the brightness of the plate is not as good as desired and above all costly final buffing is generally required.

Recently it was disclosed in Ostrow U. S. P. 2,770,587 that the presence of selenium in amounts ranging from 0.0001 to 0.01 gram per liter, in the —2 valence form, such as selenide selenium, is effective in producing very bright copper deposits from alkaline cyanide copper plating baths at current densities between about 10 to 60 amperes per square foot. Unfortunately baths containing the selenium in the—2 valence state permits practically no leveling so that the resultant copper plates require extensive mechanical buffing if they are to be overplated with smooth, mirror-like chromium or nickel coats. Further, these baths are not disclosed as permitting rapid plating at speeds above 100 amperes per square foot.

An attempt was made to combine periodic current reversal with an alkaline copper plating solution containing the sulfonic acid agent together with selenide or minus 2 selenium as well as selenate or selenite selenium (plus 6 and plus 4 valences, respectively). When these three agents were used within the proportions disclosed by the prior art only failure resulted. The use of selenide selenium with the other two agents destroys any electroleveling properties to a very large extent.

It is accordingly a major object of this invention to provide a high speed cyanide copper plating bath which will permit the formation of a smooth leveled copper plate on base metal. It is another object to devise a plating bath composition which will combine the desirable properties of the prior art baths to permit effective electroleveling of the copper plate at an acceptable high speed.

These and other objects will be apparent in the further discussion of the invention.

It has now been unexpectedly discovered that both the electro-leveling properties of cyanide copper plating baths containing selenite or selenate selenium may be combined with the high brightening effects of selenide selenium provided the selenide selenium is present in the electroplating bath in concentrations between about 0.01 and 0.1 part per million. These concentrations are well below any concentrations considered effective heretofore in copper cyanide plating baths.

The following series of examples will further illustrate the invention.

EXAMPLE 1

A four liter solution was prepared by dissolving in water the following:

	Oz.
CuCN	12
NaCN	6.5
KCN	8.5
NaOH	3.0

This solution was purified by treating it with one ounce of activated charcoal followed by filtration. Then 40 ml. of methylene-bis-α-naphthalene sulfonic acid being a 10% solution of the sulfonic acid in water to yield a concentration of one gram of the sulfonic acid per liter of bath was added. This solution was then used for plating copper in a one liter oscillating cathode cell. The cathode moved up and down at a rate equal to about 15 ft./min. of travel to provide agitation. The cathode was set at an angle such that the current density range varied from about 5 to 120 amperes per square foot from one end of the sample to the other. Total cell current was 4 amperes. A periodic current reversal cycle of 60 seconds forward (or cathodic) and 18 seconds reverse (or anodic) was used. The temperature was maintained at 78–80° C. Plating time was about 20 minutes for each sample or specimen plated. To this solution 50 parts per million (p. p. m.) of elemental selenium was added as sodium selenate. On plating from this solution the average percentage reduction in the surface roughness per mill of deposit was found to be 53 and the plate was hazy-bright. Average percentage reduction of surface roughness per mill deposit is defined as the average of several roughness values obtained at points across the operable plating range such as 5–120 amperes per square foot as given by the expression

$$\frac{I-F}{I}\times 100\times\frac{1}{T}$$

where I is the initial surface roughness, F is the final surface roughness and T is the deposit thickness in 0.001 inch. Measurement of the roughness (R. M. S.) of the surface is made with a standard surface analyzer such as the Brush surface analyzer (Brush Development Co.). The reading of the final roughness after plating is subtracted from the reading of the roughness before plating to give the percentage reduction in roughness. To this solution there was added selenide selenium in gradually increasing amounts as shown in the test runs 2–7 in Table I. The selenide solution was prepared by dissolving 0.5 gram of a solid preparation containing 5% by weight of copper selenide and 95% potassium cyanide in one liter of water. One milliliter of this solution added to one liter of plating bath was equivalent to about 0.01 part per million of selenide selenium (Se^{-2}).

Table I shows that as selenide selenium concentration approached one tenth part per million the leveling effectiveness of the plating bath was significantly decreased. A brightness above "semi-bright" or at "nearly full-bright" is quite acceptable in the trade for a copper plate. A "hazy-bright" copper plate is not acceptable.

Table I

Plating Test No.	P. p. m. Se^{-2} (Added as Cu_2Se)	Brightness	Average Percent Reduction of Surface Roughness per Mil Deposit
1	None	Hazy-bright	53
2	0.0375	Nearly full bright	54
3	0.075	Same as #2	55
4	0.10	Same as #2	38
5	0.15	Same as #2	38
6	0.30	Same as #2	42
7	0.45	Full bright	24

EXAMPLE 2

A solution was prepared as in Example 1 and plating was conducted in a four liter beaker. This solution containing selenate selenium and methylene-bis-α-naphthalene sulfonic acid but no selenide selenium, was used to plate a small "crank hole cover" of the type used on 1928 automobiles. This steel part is stamped 3.5 inches long with a 90° fold lengthwise and a width of 3 inches. At a current density of 63 amp./sq. ft. and 20 minutes of a current reversal cycle of 60 seconds forward and 18 seconds reverse the part which had been surface polished with a 220 grit Carborundum belt showed a dull finish and a roughness (R. M. S. micro inches) of 20 before plating and 16 after plating. The same solution on adding 0.05 p. p. m. Se^{-2} on another sample or part of the same shape and treatment showed a semi-bright finish and a roughness of 21 before plating and 14 after plating. Temperature of plating took place between 75 and 85° C.

EXAMPLE 3

Selenide (Se^{-2}) selenium was tested in a 300 gal. aqueous copper plating bath containing the following:

Copper cyanide	oz./gal.	11.7
Free cyanide as potassium cyanide	oz./gal.	1.35
Hydroxide as potassium hydroxide	oz./gal.	3.39
Carbonate as potassium carbonate	oz./gal.	2.62
Selenium as sodium selenate	p. p. m.	50
Methylene-bis-α-naphthalene sulfonic acid (10% aqueous solution)	ml./gal.	40

The bath was composed of both potassium and sodium salts in an approximate ratio of 1 to 1 Na to K but the salts were analyzed and calculated as potassium salts for convenience.

A bumper guard from a 1955 Chevrolet automobile (steel stamping measuring approximately 7 x 5 x 2 inches and having an effective plating surface of ¼ sq. ft.) was polished with a 220 grit Carborundum belt to produce a surface covered with visible scratches. This part was subsequently electro-cleaned, pickled, copper flashed and plated in the aforementioned bath at an applied current of 25 amps. (100 A./S. F. using a periodic reversal cycle of 60 seconds cathodic, 18 seconds anodic for 30 minutes. The bath temperature was maintained between 78 and 80° C. and the plating solution was agitated by blowing air through the solution against the part being plated from nozzles located along the bottom of the plating tank. Air was introduced at the rate of approximately 50 liters/minute. The part after plating

was hazy-bright with good leveling indicated by an almost complete disappearance of the visible polishing marks.

To the 300 gallon tank there was then added 0.05 p. p. m. selenide (Se^{-2}) selenium (3 grams of a solid mixture of 95% potassium cyanide and 5% of copper selenide). Another bumper guard, identical to the first and prepared in the same manner, was then plated under identical conditions in this bath. After plating, this piece was observed to have the same leveling qualities as the first, i. e., the disappearance of polish marks, but was considerably brighter than the first, approaching full brightness.

The cyanide copper plating baths of this invention must contain at least 10 p. p. m. of selenium as selenate or selenite selenium and may contain 250 and more p. p. m. They must also contain between about 0.01 and 0.10 p. p. m. of selenide selenium or selenium in the Se^{-2} valence state. The preferred selenide content is between 0.01 to 0.08 p. p. m. The content of methylene-bis-α-naphthalene sulfonic acid may vary between about 0.025 and 50 grams per liter since within these limits the concentration is not critical except that some of this agent must be present. These plating baths are all characterized by the presence of alkali metal cyanide such as sodium cyanide and potassium cyanide in excess of that required to form the cyanide complex with the copper cyanide. Such excess cyanide is often called "free cyanide" and is preferably equal to about one ounce of free cyanide per gallon of plating solution.

Electric current reversal plating must, of course, deposit more copper on the plated surface during the forward or cathodic part of the cycle than is removed during the reverse or anodic part of the cycle. Indeed, it is generally necessary that the forward part of the current reversible cycle be at least twice as long as the reverse or anodic part of the cycle. A forward to reverse cycle ratio of about 3 to 1 is preferred. The complete forward and reverse cycle should not be shorter than about 10 seconds and preferably not longer than about two minutes.

We claim:

1. The process for electroplating copper which comprises electrodepositing copper from an aqueous copper cyanide solution containing free cyanide selected from the group consisting of sodium cyanide and potassium cyanide, said solution containing between 0.025 to 0.5 grams per liter of an alkali metal salt of methylene-bis-α-naphthalene sulfonic acid and between about 10 and 250 p. p. m. by weight of selenium as a compound selected from the group consisting of selenates and selenites, and additionally between about 0.01 to 0.1 p. p. m. by weight of selenium as a selenide compound, subjecting said solution to a reverse current cycle of between 10 to 120 seconds' duration wherein the forward current period is at least twice as long as the reverse current period.

2. In the electrodeposition of smooth bright copper from an aqueous copper-alkali metal cyanide bath, the steps of maintaining in said bath at least 0.025 grams per liter of an alkali metal salt of methylene-bis-α-naphthalene sulfonic acid, between 10 to 250 p. p. m. by weight of selenium as a compound selected from the group consisting of selenates and selenites, and additionally between 0.01 to 0.08 p. p. m. by weight of selenium as a selenide compound and subjecting said bath to a reverse current cycle of between 10 to 120 seconds' duration wherein the forward current period is at least twice as long as the reverse current period.

3. A copper plating composition adapted to plate smooth bright copper deposits comprising an aqueous solution containing 7 to 12 oz./gal. of copper cyanide, 1 to 2 oz./gal. of an alkali metal cyanide selected from the group consisting of sodium cyanide and potassium cyanide, 1 to 8 oz./gal. of an alkali metal hydroxide selected from the group consisting of sodium hydroxide

and potassium hydroxide, 2 to 6 oz./gal. of an alkali metal carbonate selected from the group consisting of sodium carbonate and potassium carbonate, 0.025 to 0.5 gram per liter of an alkali metal salt of methylene-bis-α-naphthalene sulfonic acid, 10 to 250 p. p. m. by weight of selenium as a compound selected from the group consisting of selenates and selenites, and additionally between

about 0.01 to 0.1 p. p. m. by weight of selenium as a selenide compound.

References Cited in the file of this patent

UNITED STATES PATENTS

2,701,234	Wernlund	Feb. 1, 1955
2,732,336	Ostrow	Jan. 24, 1956