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ADDITION MATERIALS FOR IMPROVING PLATING SPEEDS

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The present invention relates to plating methods, and in particular to improved alkaline-type plating solutions and processes for plating a variety of metals, including, without limitation, cadmium, copper, gold, silver and a solderable zinc-tin alloy.

Aqueous electrolytic plating solutions may be broadly divided into two types, namely acid-type and alkaline-type solutions. Acid-type solutions or baths are usually capable of operating at comparatively high plating speeds, but frequently produce nodular deposits when operated under normal processing conditions. Alkaline-type baths are superior to acid-type baths, particularly in producing fine-grained, non-nodular deposits and possessing superior throwing power. Accordingly, in an alkaline-type plating installation precautions are not required to assure a uniform deposit; and the superior throwing power assures plating in regions which do not directly face the anode. However, the plating speed of alkaline-type electrolytes falls somewhat short of optimum requirements, particularly when compared to the high-speed plating which may be achieved with acid-type solutions.

It is an object of the present invention to provide improved plating methods and baths for increasing the plating speed of alkaline-type electrolytes. Specifically, it is within the contemplation of the present invention to provide addition materials for direct incorporation into conventional alkaline-type plating baths for increasing plating speed, without adversely affecting other desirable properties of such baths.

The speed of plating, that is the thickness of the plating deposited during a given period of time, is determined by the current density and current efficiency of an installation. In that the plating speed is directly proportional to the product of current density and current efficiency, it is possible for the plater, having a choice of working over a given range of operating current densities, to select optimum operating conditions for plating.

From the foregoing it will be appreciated that to increase the plating speed, it is necessary to increase the upper range of operating current density without a proportional loss of current efficiency; stated somewhat differently, the current value at which burning and discoloring of the plating occurs limits the maximum plating speed for a given bath.

Accordingly, it is a further object of the present invention to produce improved alkaline-type plating baths exhibiting a higher upper limit of operating current density. Additionally, the present invention contemplates the provision of plating baths which exhibit comparatively high current efficiencies over a broad range of operating current densities whereby optimum conditions of

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current density and current efficiency may be selected to achieve high-speed plating.

It is a further object of the present invention to provide addition ingredients for alkaline-type plating baths which increase plating speed, yet do not affect the surface properties or qualities of the metal platings derived from said baths.

We have found that the plating speeds of alkaline-type plating baths may be increased by the addition to said baths of at least two constituents selected from the group consisting of ammonium molybdate, gelatin and glycerin. Baths formulated according to the present invention exhibit broad ranges of operating current densities, with comparatively high upper current density limits and reasonably high efficiency over the operating current range. Although current efficiency decreases with increasing values of current densities, such decrease, as a practical matter, does not diminish the plating speed in that the plating speed is directly proportional to the current density. For example, the plating speed will double for operation at twice a given current density, although the actual plating thickness may not quite come up to the theoretical value due to the decrease in current efficiency.

Advantageously, plating speeds may be improved in accordance with the present invention for alkaline-type plating baths containing cyanide ion and hydroxide ion which are used in the electrodeposition of cadmium, copper, gold, silver, and solderable zinc-tin alloy as described in detail in copending application Serial No. 526,860, filed August 8, 1955 in the name of Edward B. Saubestre, one of the inventors herein and assigned to the assignee of the present invention.

Preferred concentrations for the several additives in their various combinations for each gallon of alkaline-type plating solutions are as follows: 1 to 3 ounces per gallon of ammonium molybdate and $\frac{1}{4}$ to $\frac{1}{2}$ ounce per gallon of gelatin; or 1 to 3 ounces per gallon of glycerin and $\frac{1}{4}$ to $\frac{1}{2}$ ounce per gallon of gelatin; or 1 to 3 ounces per gallon ammonium molybdate and 1 to 2 ounces per gallon glycerin.

The preferred concentration of ammonium molybdate and gelatin was added to a solderable high zinc-low tin alloy bath prepared in accordance with the teachings of the aforementioned copending application. The bath formulation was as follows:

Example 1

2 oz./gal. ammonium molybdate— $\frac{1}{4}$ oz./gal. gelatin in:
13.3 oz./gal. $K_2SnO_3 \cdot 3H_2O$
2.5 oz./gal. ZnO
6.3 oz./gal. KCN
4.6 oz./gal. KOH
Temperature, 65° C.

The current efficiencies for that bath formulation of Example 1 with the stated addition agents in the range of 80 to 225 amperes per square foot were as follows:

Current efficiency (per- cent).....	74	67	62	58	55	53	51
Current density (a.s.f.)....	80	100	125	150	175	200	225

The glycerin-gelatin and glycerin-ammonium molybdate addition agents in the preferred concentrations previously set forth are likewise suitable for addition to solderable zinc-tin plating baths to provide a broad range of op-

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erating current densities, with a high upper limit and reasonably high current efficiencies throughout the range. The preferred concentration of glycerin and gelatin in the solderable zinc-tin alloy plating bath is as follows:

Example 2

3 oz./gal. glycerin— $\frac{1}{2}$ oz./gal. gelatin in:
13.3 oz./gal. $K_2SnO_3 \cdot 3H_2O$
2.5 oz./gal. ZnO
6.3 oz./gal. KCN
4.6 oz./gal. KOH
Temperature, 65° C.

The current efficiencies for the plating bath of Example 2, in the operating range of current densities between 100 to 225 amperes per square foot, are as follows:

Current efficiency (percent).....	64	60	55	50	45	41
Current density (a.s.f.).....	100	125	150	175	200	225

The preferred concentration of ammonium molybdate and glycerin was added to the solderable zinc-tin plating bath in accordance with Examples 1 and 2 and the current efficiencies obtained in the range of 100–225 amperes per square foot were the same as those obtained for Example 2.

Increased plating speeds are attainable with other types of alkaline baths, the formulations of which are to be found in various plating manuals and handbooks, such as the Electroplating Engineering Handbook by A. K. Graham, published by Reinhold Pub. Co. (1955). The properties of the following baths, each of which included as an addition agent two ounces per gallon of ammonium molybdate and $\frac{1}{4}$ ounce per gallon of gelatin were investigated with the well known Hull cell operating at a current of 3 amperes. A typical cyanide-hydroxide formulation for electrodeposition of cadmium is as follows:

Example 3

Cadmium oxide—4 oz./gal. in:
Sodium cyanide, 13.1 oz./gal.
Temperature, 75° F.

Results: No burning occurred to an upper current density of approximately 175 amperes per square foot. Bright plating was achieved in the range of current densities between 100–150 amperes per square foot. Without the above addition agent, burning occurred at current densities in excess of 70–80 amperes per square foot and the plating throughout the limited operating range was dull.

A typical cyanide hydroxide plating bath for the electrodeposition of copper is as follows:

Example 4

Copper cyanide -----oz./gal.--- 8
Potassium cyanide -----do----- 12.5
Potassium carbonate -----do----- 2
Potassium hydroxide -----do----- 5.6
Temperature -----° F--- 170

Results: Increase in the plating speed with the addition agent brought about by higher current efficiency.

A typical formulation for gold plating is as follows:

Example 5

Gold (as cyanide) -----troy oz./gal.--- 1
Potassium cyanide -----oz./gal.--- 1.4
Temperature -----° F--- 150

Results: No burning of the plating up to an upper operating range of current density of approximately 175 amperes per square foot. Plating was semi-bright to bright in the range of high current densities. In the absence of the addition agent the plating burned at current densities in excess of 20 amperes per square foot.

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A typical formulation for silver plating is as follows:

Example 6

Silver cyanide -----oz./gal.--- 14
5 Potassium cyanide -----do----- 15
Potassium carbonate -----do----- 2
Potassium hydroxide -----do----- 4
Temperature -----° F--- 120

10 Results: Slight increase in useable current density before burning occurs.

A typical formulation for zinc plating is as follows:

Example 7

15 Zinc oxide -----oz./gal.--- 6
Sodium cyanide -----do----- 13
Sodium hydroxide -----do----- 6
Temperature -----° F--- 90

20 Results: Some decrease in burning at high current density, but with markedly less plating at lower current densities.

25 The foregoing results appear to indicate that the addition agents are exceptionally effective for higher ratios of cyanide to hydroxide. A ratio of cyanide content to hydroxide content for the typical formulations of Examples 3 to 7 inclusive are 6.6 for cadmium, 4.3 for copper, an intermediate high value for gold, 2.7 for silver, and 13.4 for zinc.

Although the addition agents in accordance with the present invention are useful in increasing plating speeds for all types of work processed in alkaline-cyanide plating baths, a particularly important field of application is in wire and strip plating applications. As a typical example of one wire plating application, a molybdenum wire having a diameter of .0035 inch was plated with 6% gold. Operating with a bath of the formulation according to Example 5 and using the ammonium molybdate-gelatin additive, operation was successful at current densities up to 750 amperes per square foot without appreciable change in the deposit appearance. This upper limit of operating current density and higher plating speed is far in excess of the permissible current densities for baths according to Example 5, which have been heretofore operated at current densities under 100 amperes per square foot.

What we claim is:

1. A process for plating of metals from an alkaline plating bath including cyanide ion and hydroxide ion, which comprises increasing the speed of operation of said bath by adding to said bath an addition agent, said addition agent consisting of ammonium molybdate in a concentration of one to three ounces per gallon of said bath and at least one ingredient selected from the group consisting of gelatine in the range of from one-eighth to one-half ounce per gallon of bath and glycerine in the range of from one to two ounces per gallon of bath and passing current through said bath at a current density in the range from 80 to 225 amperes per square foot of cathode.

2. In the electrodeposition of metals onto a cathodic workpiece from alkaline plating baths including cyanide ion and hydroxide ion, the steps including establishing a ratio of cyanide ion to hydroxide ion in excess of 2.7, adding to said bath an addition agent for improving the plating speed of said bath, said addition agent consisting of ammonium molybdate in the range of from 1 to 3 ounces per gallon of bath and gelatine in the range of from $\frac{1}{8}$ to $\frac{1}{2}$ ounce per gallon of bath and electrodepositing metal from said bath onto said cathodic workpiece at a current density in the range of from 80 to 225 amperes per square foot of area of said workpiece.

3. In the electrodeposition of metals onto a cathodic workpiece from alkaline plating baths including cyanide

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ion and hydroxide ion, the steps including establishing a ratio of cyanide ion to hydroxide ion in excess of 2.7, adding to said bath an addition agent for improving the plating speed of said bath, said addition agent consisting of ammonium molybdate in a concentration of from one to three ounces per gallon of bath and at least one ingredient selected from the group consisting of gelatine in the range of from one-eighth to one-half ounce per gallon of bath and glycerine in the range of from one to two ounces per gallon of bath and electrodepositing metal from said bath onto said cathodic workpiece at a

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current density in excess of 80 amperes per square foot of area of said cathodic workpiece.

References Cited in the file of this patent

UNITED STATES PATENTS

1,090,456	Darrah	Mar. 17, 1914
1,202,149	Battle	Oct. 24, 1916
2,080,520	Westbrook	May 18, 1937

FOREIGN PATENTS

515,186	Great Britain	Nov. 28, 1939
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