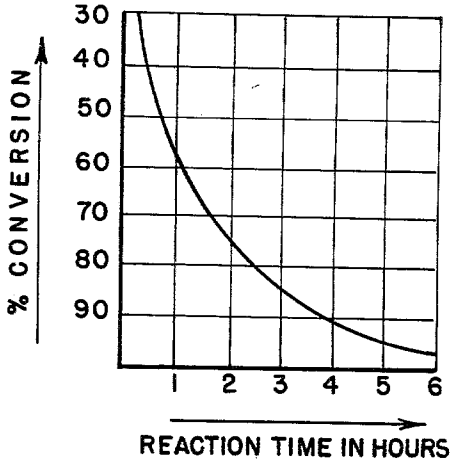
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PROCESS AND BATH FOR ELECTROLYTIC COPPER DEPOSITION

Filed Oct. 12, 1961

% CONVERSION VERSUS TIME AT 115–120° F



INVENTORS
PETER LEENDERS
HANS GERD CREUTZ

BY Cushman, Darby & Cushman
ATTORNEYS

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PROCESS AND BATH FOR ELECTROLYTIC COPPER DEPOSITION

Peter Leenders, Allendale, N.J., and Hans G. Creutz, Detroit, Mich., assignors to Allied Research Products, Incorporated, Baltimore, Md., a corporation of Maryland

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This application is a continuation-in-part of our copending application Serial No. 46,102, filed July 29, 1960, now Patent Number 3,084,112.

The present invention relates to electro-depositing copper from an aqueous alkaline cyanide copper plating bath and to improved compositions for such baths.

The aqueous alkaline cyanide plating bath serves for "copper-striking" steel, which cannot be plated with an adherent deposit from an acid bath, the initial plating of zinc die castings, for plating an undercoat of copper before nickel plating and for plating various other base metals. A typical formulation for such baths comprises copper cyanide, potassium cyanide and sodium hydroxide.

Among the disadvantages of the cyanide bath is included the accumulation of sodium carbonate, a by-product of sodium cyanide decomposition, which results in decreased anode efficiency. It has been proposed to control such accumulation by, for example, freezing out the carbonate through cooling to 30° F. or by precipitation by adding certain calcium salts. However, the freezing out operation as well as the precipitation methods are cumbersome and expensive.

Metallic impurities in cyanide baths known to be harmful include chromium Cr^{+6}, which reduces cathode efficiency and may result in blistering or peeling of any subsequent plate. The chromium may be reduced with sodium hydrosulphite, but again, sulphur thereby introduced into the bath is highly undesirable.

It is therefore an object of this invention to eliminate the disadvantages normally associated with the use of alkaline cyanide copper plating baths.

Another object of this invention is to eliminate undesirable sodium carbonate accumulation in such baths.

An additional object of this invention is to increase the anode efficiency in such baths.

A further object of this invention is to reduce the hexavalent chromium content of alkaline cyanide copper plating baths.

It is a still further object of this invention to provide such baths having good chelating and complexing properties for most two and three valent metals.

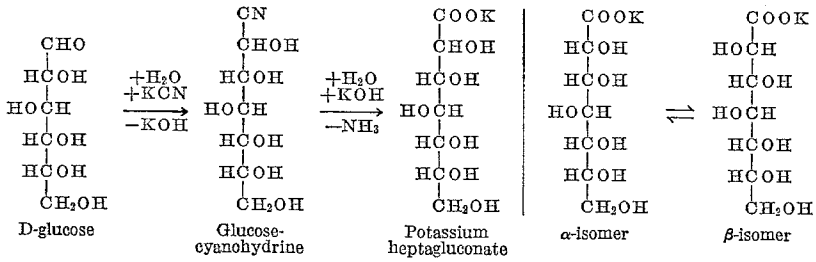
Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter, it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by incorporating in the alkaline cyanide copper plating bath a sugar heptonic acid. As the sugar heptonic acid there can be employed α-heptagluconic acid, β-heptagluconic acid, α-manno-heptonic acid, α-galacto-heptonic acid, β-galacto-heptonic acid, fructoheptonic acid and rhamnoheptonic acid. Both the D and L forms of the sugar acids can be employed. The sugar acids are normally employed as their alkali metal salts, e.g., sodium heptagluconate and potassium heptagluconate. Even if the free sugar acid is employed, it is converted to the alkali metal salt in the cyanide bath.

These sugar heptonic acids and the alkali salts thereof were disclosed in the copending application Serial No. 46,102 as additives to eliminate staining and other undesirable effects caused by the incorporation of acetylenic brighteners in aqueous alkaline cyanide copper plating baths. We have now found that the sugar heptonic acids may be effectively used alone as additives.

The preferred sugar acid material is a mixture of potassium α D-heptagluconate and potassium β D-heptagluconate made by reacting D-glucose with potassium cyanide and hydrolizing the glucose cyanohydrine.

A simplified reaction scheme is as follows:



This material is identified as potassium heptagluconate in Example 2. In place of the potassium salt, sodium heptagluconate can be employed with similar effect.

Example 1

Ingredient	Pounds	Grams/Liter
Dextrose monohydrate	1,500	399
Potassium cyanide	500	133
Water to make 450 gallons.		

250 gallons of water was placed in a tank and the dextrose monohydrate added and dissolved. The potassium cyanide was then added together with enough water to bring the total volume to 450 gallons. The ensuing reaction was slightly exothermic and the temperature rose slowly and remained within the range of from 115° to 120° F. The mixture was agitated and after about 90% of the material was converted (determined by titrating the free cyanide remaining and/or by calculating the amount of unreacted dextrose with Fehling's solution) 25 pounds of potassium cyanide was added to speed up the reaction. When less than 40 grams per liter of unreacted dextrose was left in the product the solution was heated to boiling for about one hour to hydrolyze the glucose cyanohydrine and to drive off the ammonia. After cooling to about 170° F. 60 pounds of 35% hydrogen peroxide was added and the mixture cooled to room temperature and stored.

In the foregoing example the reaction temperature may vary between 90° and 130° F. and the amount of hydrogen peroxide used may range between about 50 and

100 pounds of the 35% solution. It is to be understood that sodium heptagluconate may be prepared from dextrose and sodium cyanide and that salts of other sugar heptonic acids may be similarly produced.

As illustrative of the reaction activity in the production of the potassium salt, there is shown in the single figure of the accompanying drawing a curve, the ordinates of which are given in terms of percent conversion of the glucose to glucose cyanohydrine and the abscissae in terms of reaction time in hours. The curve was constructed from values attained in Example 1. The curve was plotted for a reaction time of four hours and slopes sharply at first and then more gradually after a reaction time of about two hours until a 90% conversion value is reached.

Among the outstanding properties of the alkali metal heptagluconates are:

(1) Improved chelating and complexing properties for most two and three valent metals.

(2) Improved effectiveness in anode depolarization.

(3) Brightening effect.

(4) Effective depression of reverse leveling caused by many primary brighteners.

(5) Ability to reduce hexavalent chromium.

(6) Ability to produce smooth grain refined deposits.

The alkali cyanide copper plating bath can be that in standard operation other than for the above additive. Such baths usually contain from 20 to 75 grams per liter of copper and from 45 to 145 grams per liter of an alkali metal cyanide. While the sugar heptonic acid can be employed in an amount of from 1.0 to 100 grams per liter, it is usually employed in an amount of from 10 to 60 grams per liter.

Typical ranges of materials and conditions are:

Copper cyanide ____grams/liter__	30 to 90
Potassium cyanide ____do____	45 to 145
Potassium hydroxide ____do____	7.5 to 37.5
pH ____do____	12 to 14
Temperature ____° F__	100 to 175
Cathode current density ____amperes/sq. ft__	1 to 80
Anode current density ____do____	1 to 30
Potassium heptagluconate ____grams/liter__	10 to 60
Potassium carbonate ____do____	0 to 110
Rochelle salt ____do____	0 to 45

As a result of the present invention smooth copper electrodeposits are obtained from alkaline cyanide copper plating solutions on conventional base metals such as iron, steel, nickel, lead, copper and alloys, e.g., brass. With steel or zinc preferably the base metal is given an initial thin flash of copper from a low efficiency cyanide copper bath.

In the specification and claims, all proportions are by weight unless otherwise indicated.

In Examples 2 and 3, the anode and cathode efficiencies of baths containing alkali heptagluconates were determined. The plating operations were carried out in a 450 ml. test cell having brass cathodes at a temperature of 150° F.

Wetting agents can be added such as lauryl oxyethylsulphate, nonylphenol-polyethylene oxide, sodium toluene sulphonate, potassium naphthalene bismethylene sulphonate or certain cationic wetting agents.

In the examples, remarkably good anode efficiencies were obtained over a current density range from 25–40 amperes/sq. ft. The anode efficiencies can further be improved if a combination of heptagluconates with other complexing or chelating agents, such as ethylene diamine tetracetic acid or Rochelle salt is used, with the heptagluconate being the main constituent in this combination.

Example 2

Material:	Proportions (Pounds)
Rochelle salt	170
Sodium benzoate	1
EDTA (40%)	40
Dextrose	9
Potassium heptagluconate (of 50% solution)	730
Water to make 100 gallons.	

Example 3

Material:	Proportions (Pounds)
Sodium benzoate	1
EDTA (40%)	40
Dextrose	8
Potassium heptagluconate (of 50% solution)	115
Water to make 115 gallons.	

The materials prepared in Examples 2 and 3 were incorporated in amounts of 5% by weight in plating baths containing:

CuCN	oz./gal__	8.0
KCN	do____	1.3
NaOH	do____	1.8

The results of the efficiency tests, all of which were run without agitation, are given in Table I.

TABLE I

Time (minutes)	Current Density (A./Ft.²)	Additive	Percent anode efficiency	Percent cathode efficiency	Temp., ±2° F.
10	25	5%, 2____	91.1	93.1	150°
10	30	5%, 2____	75.1	85.8	150°
10	40	5%, 2____	49.5	75.6	150°
10	25	5%, 3____	86.5	89.8	150°
10	30	5%, 3____	69.3	87.2	150°
10	40	5%, 3____	36.1	80.5	150°

The addition of an alkali metal heptagluconate to an aqueous alkaline cyanide copper plating bath increases the anode efficiency in the solution and gives a smoother copper deposit. This is due to the effect of the heptagluconate of minimizing the roughness-causing films produced by the anodes. In addition, deleterious effects of metallic contaminants capable of interfering with the performance of conventional metallic or organic brighteners are also minimized.

We claim:

1. An aqueous alkaline cyanide copper plating solution consisting essentially of 20 to 75 grams per liter of copper cyanide, 40 to 145 grams per liter of an alkali metal cyanide and 1 to 100 grams per liter of alkali metal salt of sugar heptanoic acid.

2. An aqueous alkaline cyanide copper plating solution of claim 1 wherein said alkali metal salt of sugar heptanoic acid is sodium heptagluconate.

3. An aqueous alkaline cyanide copper plating solution of claim 1 wherein said alkali metal salt of sugar heptanoic acid is potassium heptagluconate.

4. A process for producing a smooth copper electroplate which comprises electroplating copper from an aqueous alkaline cyanide copper plating bath consisting essentially of 20 to 75 grams of copper cyanide, 40 to 145 grams per liter of an alkali metal cyanide and 1 to 100 grams per liter of an alkali metal salt of sugar heptanoic acid.

5. The process of claim 4 wherein the alkali metal salt of sugar heptanoic acid is sodium heptagluconate.

6. The process of claim 4 wherein the alkali metal salt of sugar heptanoic acid is potassium heptagluconate.

(References on following page)

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References Cited by the Examiner

UNITED STATES PATENTS

694,658	3/1902	Meurant	204—52
2,443,600	6/1948	Chester	204—52
2,840,605	6/1958	Leonard	260—528
2,861,928	11/1958	Ceresa et al.	204—52
2,861,929	11/1958	Martin et al.	204—52
2,881,211	4/1959	Sperry	260—528
3,030,281	4/1962	Moy	204—52

6

OTHER REFERENCES

Fieser, "Organic Chemistry," Reinhold Publishing Corp., 1956, pages 350–351.

"Ind. Eng. Chem." (Mehltretter et al.) 45:2782 (1953).

Lucas Organic Chemistry, 2nd Edition, 1953, American Book Co., pages 613–622.

JOHN H. MACK, *Primary Examiner.*

MURRAY TILLMAN, *Examiner.*