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ELECTROPLATING ELECTROLYTES

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This invention relates, in general, to novel electroplating brightener materials, electrolyte compositions and methods of electroplating. More particularly, this invention relates to novel ester products which have utility as additives to nickel, cobalt, nickel-cobalt and copper plating electrolytes.

Bright nickel, cobalt and nickel-cobalt alloy coatings may be achieved by buffing dull electrodeposits to a high luster. However, certain organic compounds may be added to standard plating baths to produce bright deposits initially and eliminate the necessity for buffing. Such baths are known as bright plating baths and the additives are known as brighteners. The formulation of bright plating baths is complex and the complexity is compounded by further additions or formulations to make the deposit ductile and to attain a leveling action in the bath in order to cover surface imperfections, all in a wide current density range.

Addition agents are also employed in copper plating electrolytes for grain refinement, brightness, leveling and to improve other properties of the copper deposit. Some addition agents contain sulfur and while they function effectively as brightening agents the code position of sulfur tends to make the copper deposits brittle. Other additives are effective grain refining agents at lower temperatures but lose their effectiveness at elevated temperatures.

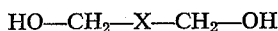
Accordingly, it is the general object of this invention to provide a new class of materials which may be employed as additives in copper, nickel, cobalt and nickel-cobalt alloy electroplating baths.

A more specific object of this invention is to provide electrolytes from which bright, ductile and leveled nickel, cobalt and nickel-cobalt alloying coatings may be electrodeposited easily and consistently.

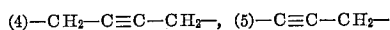
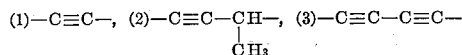
Another object of this invention is to provide methods for electrodepositing bright, ductile and leveled coatings of nickel, cobalt and nickel-cobalt alloys.

Yet another object of this invention is to provide electrolytes and methods for electrodepositing fine grained, lustrous and ductile copper coatings over a wide plating bath temperature range.

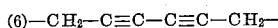
It has now been discovered that a novel class of materials may be prepared by the reaction of (A) a hydroxy or amine substituted aliphatic carboxylic acid having from two to four carbon atoms with (B) at least one acetylenic dibasic alcohol having not more than eight carbon atoms. The alcohols have the structural formula:



in which X is selected from the group consisting of:



and



Examples of suitable acids include glycine and β -alanine and lactic, α -hydroxy propionic, β -hydroxy propionic, α -hydroxy- γ -amino butyric, malic, glycolic, tartaric, β -hydroxy butyric and aspartic acids.

Acetylenic dibasic alcohols having not more than eight carbon atoms and a structure in which the hydroxyl

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groups are attached to the terminal carbon atoms and the acetylenic bond is not associated with the terminal carbon atoms may be employed. Examples of suitable alcohols include butynediol, octadiynediol, 3-methylpentynediol-2, hexadiyne-2,4-diol-1,6, hexa-3-yne-1,6-diol and pentyne-1,5-diol.

The reaction is conducted in an aromatic hydrocarbon liquid. The charge of acid and alcohol is refluxed in a vessel equipped with a water trap. After the reaction is completed, i.e., when the theoretical water of condensation has been accumulated in the trap, the aromatic hydrocarbon in the reacted charge is removed by vacuum evaporation. The residue is diluted with water and carbon treated to remove traces of the aromatic hydrocarbon and other impurities. This reaction product, without further purification, may be added to electroplating baths as a brightening agent. It is believed that the reaction product is essentially or primarily the ester of the described hydroxy and/or amino substituted acids and the described acetylenic alcohols. It is also believed that these esters are efficacious brighteners as described hereinbelow. Side reactions apparently take place and, as noted, the reaction product itself may be employed to avoid the cost of purification.

The following examples will specifically illustrate the reaction product brighteners, electrolytes and plating methods in accordance with this invention but should not be considered as limitations on the scope of the invention.

Example I

About 0.1 mole of glycine and 0.1 mole of butynediol are intimately mixed and placed in a 500 ml. flask. The mixture is covered with 300 ml. of dry toluene. The flask is fitted with a water trap and a reflux condenser. The reaction mixture is refluxed for 40 hours. During this time, about 0.1 mole of water is collected in the water trap. The toluene is decanted from the brown residue in the flask. The residual toluene is then removed by vacuum stripping. The residue in the flask is dispersed in water and filtered to remove the insoluble polymeric material. The resultant brown musty smelling liquid is employed as an additive to electroplating baths or electrolytes as outlined in the examples hereinbelow.

Example II

About 1 mole of threonine and 1 mole of octadiynediol are reacted in the manner outlined in Example I, hereinabove. The resulting tan solution is employed as an additive in the examples outlined hereinbelow.

Example III

About 0.15 mole of alanine is ground together with 0.1 mole of sublimed butynediol. The mixture is placed in a 500 ml. flask and covered with 300 ml. of dry benzene. The reaction mixture is distilled until about 0.1 mole of water is collected in the water trap. The benzene is removed by distillation under reduced pressure. The resulting brown solid is dispersed in water, carbon treated and filtered. The product is a brown solution and is employed as an additive to electroplating baths in the examples hereinbelow.

Example IV

About 1.5 mole of β -aminobutyric acid and 1 mole of butynediol are reacted in toluene until 1.3 mole of water is collected in the water trap. The toluene is decanted and stripped from the solid by vacuum distillation. The residue is dispersed in water. The solution is filtered and the filtered solution is employed as an additive in the examples below.

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Example V

About 0.8 mole of β -aminopropionic acid and 1 mole of butynediol are reacted in xylene by refluxing the charge for about 60 hours. In this time, about 0.85 mole of water is collected in the trap. The xylene is decanted. The residual xylene is vacuum stripped and the residue is dispersed in water. The solution is filtered and the filtered solution is employed as an additive in the examples below.

Example VI

About 0.11 moles of butynediol and 0.1 mole of potassium acid tartrate are placed in the reaction vessel and covered with chlorobenzene. An azeotropic water trap is attached to the vessel to collect the water formed by the esterification. The refluxing is continued until no further water is evolved. The chlorobenzene is decanted and the reacted mass is dried at 100° C., under vacuum. The residual solid is dissolved in water and filtered. A light tan solution results and is employed as an additive to electroplating baths in the examples hereinbelow.

The foregoing materials are incorporated into plating baths as illustrated by the following specific examples:

Example VII

NiSO ₄ ·6H ₂ O	oz./gal.	40.0
NiCl ₂ ·6H ₂ O	oz./gal.	6.5
H ₃ BO ₃	oz./gal.	5.0
Reaction product of glycine and butyne-		
diol, based on 100% solids	oz./gal.	0.002
Temperature	° F.	150
pH		3.4

A 3-ampere Hull Cell panel is plated for 5 minutes from this bath. The nickel electrodeposit is hazy-bright, leveled and fairly ductile.

Example VIII

NiSO ₄ ·6H ₂ O	oz./gal.	40.0
NiCl ₂ ·6H ₂ O	oz./gal.	6.0
H ₃ BO ₃	oz./gal.	5.0
Reaction product of potassium acid tar-		
trate and butynediol, based on 100%		
solids	oz./gal.	0.05
Temperature	° F.	150
pH		3.8

A 3-ampere Hull Cell panel is plated from this bath. The panel is bright and leveled in the current density range of 10 to 140 amps./sq. ft. Moreover, the electrodeposit was highly ductile.

Example IX

NiCl ₂ ·6H ₂ O	oz./gal.	30
H ₃ BO ₃	oz./gal.	5.5
Disodium salt of 2,5-benzenedisulfonic		
acid	oz./gal.	3.0
Saccharin	oz./gal.	0.1
Reaction product of threonine and octa-		
diynediol, based on 100% solids	oz./gal.	0.0015
Temperature	° F.	150
pH		3.8

The deposit of nickel from this bath will be full-bright in the range of 5 to 300 amp./sq. ft. The deposit will be ductile and have a fair degree of leveling.

Example X

CoSO ₄ ·7H ₂ O	oz./gal.	65
NaCl	oz./gal.	2
H ₃ BO ₃	oz./gal.	6
Reaction product of malic acid and octa-		
diynediol, based on 100% solids	oz./gal.	0.03
Temperature	° F.	140
pH		3.8

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A leveled and fairly ductile deposit is obtained. The deposit will be bright in the current density range from 10 to 200 amps./sq. ft.

Example XI

NiSO ₄ ·6H ₂ O	oz./gal.	32
NiCl ₂ ·6H ₂ O	oz./gal.	4
CoSO ₄ ·7H ₂ O	oz./gal.	0.4
H ₃ BO ₃	oz./gal.	4
(NH ₄) ₂ SO ₄	oz./gal.	0.1
Sodium salt of 2,7-naphthalenedisulfonic		
acid	oz./gal.	2.0
Reaction product of alanine and bu-		
tynediol, based on 100% solids	oz./gal.	0.2
Temperature	° F.	140
pH		3.8

The nickel-cobalt alloy electrodeposit on a 3-ampere Hull Cell panel is full-bright and leveled.

Example XII

NiSO ₄ ·6H ₂ O	oz./gal.	40.0
NiCl ₂ ·6H ₂ O	oz./gal.	6.0
H ₃ BO ₃	oz./gal.	5.0
Trisodium-1,3,6-naphthalenetrisulfonic		
acid	oz./gal.	3.0
Saccharin	oz./gal.	0.15
Reaction product of glycine and butyne-		
diol, based on 100% solids	oz./gal.	0.015
Temperature	° F.	150
pH		3.55

The deposit from this bath is mirror-bright and highly leveled over a current density range of 10 to 350 amps./sq. ft. Moreover, the deposit is ductile.

The concentration of the described class of reaction products should range from about 0.001 to 0.02 ounce per gallon when employed in nickel, cobalt or nickel-cobalt alloy plating electrolytes. The foregoing concentration range should be employed both with and without additional additives. Additional additives, known in the art and to be described hereinafter may be employed to further improve other properties of the deposit. A concentration below about 0.001 ounce per gallon will not produce a significant improvement in brightness while concentrations above about 0.02 ounce per gallon, especially in the absence of other additives such as saccharin and the sodium styrene sulfonate to be described hereinbelow, may produce deposits with evidence of stress-cracking. The optimum concentration range is from about 0.004 to 0.01 ounce per gallon.

It has also been discovered that sodium styrene sulfonate is effective in brightening the deposits of nickel, cobalt and nickel-cobalt alloys from their respective electrolytes. A full-bright leveled but somewhat brittle electrodeposit is produced in standard baths with no other additives. Other additives, as for example saccharin, may be employed in combination with the sodium styrene sulfonate to further improve the properties of the deposit. Saccharin, for example, will further improve the leveling power of the bath.

The combination of sodium styrene sulfonate and the heretofore described reaction product additives produce especially desirable and surprisingly attractive electrodeposits of nickel, cobalt and nickel-cobalt alloys. A mirror-bright, ductile, leveled deposit with a surprising depth of color will be produced by electrolytes employing this combination of additives. The concentration of sodium styrene sulfonate, both with and without additional additives should range from about 0.005 to 1.0 ounce per gallon, the optimum range being from about 0.01 to 0.75 ounce per gallon.

For example, nickel may be plated in accordance with the following specific illustrations.

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Example XIII

NiSO ₄ ·6H ₂ O	oz./gal.	40.0
NiCl ₂ ·6H ₂ O	oz./gal.	6.5
H ₃ BO ₃	oz./gal.	5.0
Saccharin	oz./gal.	0.134
Sodium styrene sulfonate	oz./gal.	0.5
Temperature	° F.	150
pH		3.8

A 3-ampere Hull Cell panel is plated in this bath for five minutes. A full-bright, leveled but somewhat brittle electrodeposit is produced.

Example XIV

NiSO ₄ ·6H ₂ O	oz./gal.	40.0
NiCl ₂ ·6H ₂ O	oz./gal.	6.5
H ₃ BO ₃	oz./gal.	5.0
Saccharin	oz./gal.	0.134
Reaction product of glycine and butynediol, based on 100% solids	oz./gal.	0.004
Sodium styrene sulfonate	oz./gal.	0.01
Temperature	° F.	150
pH		3.8

A 3-ampere Hull Cell panel is plated in this bath for five minutes. The panel is mirror-bright, highly leveled and ductile. The bath has excellent throwing power.

I have also discovered that the reaction product of glycine and butynediol is an effective grain refining agent in copper electrolytes. In copper plating baths, the concentration of the glycine-butynediol reaction product should range from about 0.002 to 0.07 ounce per gallon and preferably from about 0.004 to 0.05 ounce per gallon. This additive is an effective grain refining agent at elevated temperatures, e.g. at 140° F., where some other additives lose their efficacy.

For example, copper may be plated in accordance with the following specific illustration.

Example XV

CuSO ₄ ·5H ₂ O	oz./gal.	28.0
H ₂ SO ₄	oz./gal.	8.0
Dextrin	oz./gal.	0.016
Reaction product of glycine and butynediol, based on 100% solids	oz./gal.	0.016
Temperature	° F.	140

A 3-ampere Hull Cell panel is plated from the above bath. The panel is ductile, finely grained and semi-bright. The bath has excellent throwing power.

While there have been shown and described what are presently considered to be the preferred embodiments of the invention, modifications thereto will readily occur to those skilled in the art. It is not desired, therefore, that the invention be limited to the specific arrangements shown and described and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

I claim as my invention:

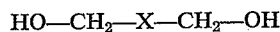
1. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and as brightener an effective amount of the product of the reaction of (A) a substituted aliphatic carboxylic acid having from 2 to 4 carbon atoms and at least one substituent selected from the group consisting of hydroxyl and amino groups and (B) an acetylenic dibasic alcohol having not more than 8 carbon atoms, not more than two triple bonds, and a structure in which the hydroxyl groups are attached to the terminal carbon atoms and the acetylenic bond is not associated with the terminal carbon atoms.

2. The acidic solution of claim 1 in which said brightener is present in a concentration of about 0.001 to 0.02 ounce per gallon of solution.

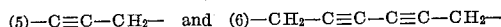
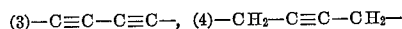
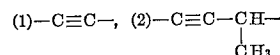
3. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt

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and nickel-cobalt alloys containing a soluble salt of said metal and as brightener an effective amount of the product of the reaction of (A) a substituted aliphatic carboxylic acid having from 2 to 4 carbon atoms and at least one substituent selected from the group consisting of hydroxyl and amino groups and (B) an acetylenic dibasic alcohol containing not more than 8 carbon atoms and having the formula:



10 in which X is selected from the group consisting of



4. The acidic solution of claim 3 in which said brightener is present in a concentration of about 0.001 to 0.02 ounce per gallon of solution.

5. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and (1) as brightener an effective amount of the product of the reaction of (A) a substituted aliphatic carboxylic acid having from 2 to 4 carbon atoms and at least one substituent selected from the group consisting of hydroxyl and amino groups and (B) an acetylenic dibasic alcohol having not more than 8 carbon atoms, not more than two tripple bonds, and a structure in which the hydroxyl groups are attached to the terminal carbon atoms and the acetylenic bond is not associated with the terminal carbon atoms and (2) sodium styrene sulfonate.

6. The acidic solution of claim 5 in which the brightener (1) is present in a concentration of about 0.001 to 0.02 ounce per gallon of solution and the sodium styrene sulfonate (2) is present in a concentration of about 0.005 to 1.0 ounce per gallon of solution.

7. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt, nickel-cobalt alloys and copper containing a soluble salt of said metal and as brightener an effective amount of the product of the reaction of (A) glycine and (B) butynediol.

8. An aqueous acid solution for electrodepositing copper containing a soluble salt of copper and from about 0.002 to 0.07 ounce per gallon of solution of the product of the reaction of (A) glycine and (B) butynediol.

9. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and from about 0.001 to 0.02 ounce per gallon of solution of the product of the reaction of (A) glycine and (B) butynediol.

10. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and as brightener an effective amount of the product of the reaction of (A) potassium acid tartrate and (B) butynediol.

11. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and as brightener an effective amount of the product of the reaction of (A) threonine and (B) octadiynediol.

12. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and as brightener an effective amount of the product of the reaction of (A) alanine and (B) butynediol.

13. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and as brightener an effective amount of the prod-

uct of the reaction of (A) malic acid and (B) octadiyne-diol.

14. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and (1) as brightener an effective amount of the product of the reaction of (A) glycine and (B) butyne-diol and (2) sodium styrene sulfonate.

15. An aqueous acidic solution for electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys containing a soluble salt of said metal and (1) as brightener an effective amount of the product of the reaction of (A) threonine and (B) octadiynediol and (2) sodium styrene sulfonate.

16. A method of electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys comprising the steps of electrolyzing an aqueous acidic electrolyte containing a soluble salt of said metal and (1) as brightener an effective amount of the product of the reaction of (A) a substituted aliphatic carboxylic acid having from 2 to 4 carbon atoms and at least one substituent selected from the group consisting of hydroxyl and amino groups and (B) an acetylenic dibasic alcohol having not more than 8 carbon atoms, not more than two triple bonds, and a structure in which the hydroxyl groups are attached to the terminal carbon atoms and the acetylenic bond is not associated with the terminal carbon atoms and (2) sodium styrene sulfonate.

17. A method of electrodepositing a metal selected from the group consisting of nickel, cobalt and nickel-cobalt alloys comprising the steps of electrolyzing an aqueous acidic electrolyte containing a soluble salt of said

metal and as brightener an effective amount of the product of the reaction of (A) a substituted aliphatic carboxylic acid having from 2 to 4 carbon atoms and at least one substituent selected from the group consisting of hydroxyl and amino groups and (B) an acetylenic dibasic alcohol having not more than 8 carbon atoms, not more than two triple bonds, and a structure in which the hydroxyl groups are attached to the terminal carbon atoms and the acetylenic bond is not associated with the terminal carbon atoms.

18. A method of electrodepositing copper comprising the steps of electrolyzing an aqueous acidic electrolyte containing a soluble copper salt and as brightener an effective amount of the product of the reaction of (A) glycine and (B) butynediol.

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