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ELECTRODEPOSITION OF METALS

Henry Brown, Kansas City, Mo., assignor to The Udylite Corporation, Detroit, Mich., a corporation of Delaware

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My invention relates to improvements in the electrodeposition of metals. It is particularly concerned with the utilization of certain addition agents, for the purposes hereinafter stated, in aqueous acidic electroplating baths.

I have discovered that certain substances, hereinafter described in detail, when added to electroplating baths, particularly aqueous acidic electroplating baths such as used for the electrodeposition of nickel, cobalt, iron, zinc, cadmium, copper, antimony, various alloys containing the aforementioned and other metals, and the like, are remarkably effective in the prevention of the formation of pits in the electro-deposited coatings, said pits normally being caused by the adherence of gas bubbles during the electrodeposition of the coating. I have found, further, that this result is accomplished despite the fact that very low concentrations of the addition substances are employed and, still further, that these results are accomplished without causing any significantly appreciable interference with the desired appearance, structure, and character of the plate.

I have also discovered that the addition agents are highly effective independently of whether various organic or inorganic so-called brightening agents are also present in the electrolyte bath. Various addition agents have heretofore been suggested for reducing or eliminating pitting in electrodeposition operations but, at least in most cases, and apart from other deficiencies which they possess, they have proven to be wholly unsatisfactory where the electrodeposition bath contained brighteners. Thus, for example, in baths employed for the electrodeposition of bright nickel, where the brightening agent comprises an aryl sulphonic acid, for example, naphthalene 1,5 disulphonic acid, sodium salt, or sulphonamides or sulphonimides such as are disclosed in my Patent No. 2,191,813, issued February 27, 1940, various suggested anti-pitting agents have proven entirely unsatisfactory. The use of the addition agents in bright plating baths represents but one aspect of my present invention although, to be sure, a highly important one.

The addition agents which I have found to be unusually satisfactory, in accordance with my present invention, can be used in sufficiently low concentrations so as to reduce substantially, or eliminate entirely, pitting of the deposits and, at the same time, they do not interfere to any significantly appreciable extent with the particular cathodic process involved such as reduction of inorganic or organic substances taking place in the process of electrodepositing the coating. This is highly important where the deposited metal is desired not only free from pits but also of maximum ductility and purity and freedom from such inclusions as sulphur, carbon and colloids. It is also of considerable importance in those cases involving bright plating baths, particularly aqueous acid plating baths for the electroplating of nickel, which baths contain brighteners such as those mentioned hereinabove, particularly those wherein the brightener is in the form of a soluble compound containing the radical $—SO_2.N=$. As I have pointed out hereinabove, the brightness or brilliance or high luster of the deposits is not adversely affected where the addition agents, to which my present invention relates, are employed.

The novel and highly useful addition agents which accomplish the functions set out hereinabove are, in general, sulpho-carboxylic acid esters, particularly, sulpho-fatty acid esters, of water-soluble polyhydric alcohols partially esterified with aliphatic carboxylic acids, particularly fatty acids, containing from 8 to 18 carbon atoms. The sulpho-carboxylic radical contains from 2 to 6 carbon atoms, the sulphoacetates being particularly satisfactory. In place of the higher molecular weight fatty acid acyl radical, a corresponding alkyl radical may be utilized in which event the compounds would contain an ether radical.

Illustrative examples of addition agents which may be utilized in accordance with my invention and in the concentrations which are, in general, preferred, are shown in Table I:

Table I

	Anion	Cation	Conc., grams/liter
1	$CH_3-(CH_2)_6-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-SO_3-$ (Capric acid ester of ethylene glycol sulphoacetate)	H+, Na+ or metal of bath being used	0.1-0.5
2	$CH_3-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-SO_3-$ (Lauric acid ester of trimethylene glycol sulphoacetate)	do	0.1-0.5
3	$CH_3-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{OH}{CH}-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-SO_3-$ (Lauric acid mono-ester of glycerol mono-sulphoacetate)	do	0.1-0.5
4	$CH_3-(CH_2)_{12}-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-SO_3-$ (Myristic acid ester of ethylene glycol sulphopropionate)	do	0.05-0.5
5	$CH_3-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O-C_2H_4-O-C_2H_4-O-\overset{O}{\overset{\|}{C}}-CH_2-SO_3-$ (Lauric acid ester of diethylene glycol sulphoacetate)	do	0.05-0.5
6	$CH_3-(CH_2)_{10}-CH_2-O-CH_2-\underset{OH}{CH}-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-SO_3-$ (Lauryl mono-ether of glycerol mono-sulphoacetate)	do	0.05-0.5
7	$CH_3-(CH_2)_6-CH_2-O-C_2H_4-O-C_2H_4-O-\overset{O}{\overset{\|}{C}}-CH_2-SO_3-$ (Octyl ether of diethylene glycol sulphoacetate)	do	0.05-0.5
8	$CH_3-(CH_2)_6-\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{OH}{CH}-CH_2-O-\overset{O}{\overset{\|}{C}}-CH_2-SO_3-$ (Caprylic acid mono-ester of glycerol mono-sulphoacetate)	do	0.05-0.5

The water-soluble aliphatic polyhydric alcohols, the specific derivatives of which comprise the addition agents of my present nvention, may be selected from a large class and include, for example, glycerin; glycols such as ethylene glycol, propylene glycol, trimethylene glycol, and the like; polyglycols such as diethylene glycol, triethylene glycol, and the like; polyglycerols such as diglycerol, triglycerol, tetraglycerol and mixtures thereof; carbohydrates and sugars such as dextrose, sucrose, and maltose; and sugar alcohols such as arabitol, mannitol, sorbitol, dulcitol, mannitan and sorbitan, and the like.

The aliphatic carboxylic acids with which the aforementioned or similar water-soluble aliphatic polyhydric alcohols are esterified may also be selected from a large group including, by way of illustration, caprylic acid, nonylic acid, capric acid, undecylic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, ricinoleic acid, mixtures of any two or more of the above-mentioned or other acids; mixed fatty acids, containing from 8 to 18 carbon atoms, derived from animal or vegetable sources as, for example, lard, coconut oil, sesame oil, rapeseed oil, palm kernel oil, palm oil, olive oil, corn oil, cottonseed oil, sardine oil, tallow, soya bean oil, peanut oil, castor oil, seal oils, whale oil, shark oil and other fish oils and partially or completely hydrogenated animal and vegetable oils such as those mentioned. I prefer particularly to use the straight chain, unsubstituted aliphatic carboxylic acids, especially the fatty acids, but, in certain instances, branched-chain and substituted, for example, the alpha-hydroxy derivatives of the aforementioned acids, may be utilized. Any of the carboxylic acids listed hereinabove may be esterified with any of the listed polyhydric alcohols to form partial esters, the sulphocarboxylic acid esters of which comprise the addition agents used in accordance with the present invention.

Where the ethers of the aliphatic polyhydric radicals are employed, they may be prepared from the alcoholates of the alcohols corresponding to the aliphatic and fatty carboxylic acids listed hereinabove. Examples 6 and 7 in Table I are illustrative of ether derivatives which may be used in the practice of my present invention.

The sulphocarboxylic acid radical, as pointed out hereinabove, should contain not more than six carbon atoms. Especially satisfactory are the sulphoacetates, although sulphopropionates, sulphobutyrates, sulphovalerates, sulphoacrylates, and the like may also be utilized.

It will be understood that the sulphocarboxylic acid radical is linked to the remainder of the molecule of the addition agent through an hydroxy group of the aliphatic polyhydric alcohol radical. The molecule of the addition agent may contain one or more aliphatic or fatty acid alkyl or acyl radicals and one or more sulphocarboxylic acid groups. Of especial utility are the sulphoacetates of glycerin and glycol partial esters of lauric acid or coconut oil mixed fatty acids or special fractions particularly high in content of lauric acid.

The addition agents are utilized preferably in the form of their free acids or their alkali metal salts or in the form of a salt of the metal to be electrodeposited. In most cases, it is preferable to utilize the sodium salt.

The addition agents are employed in concentrations of the general order of about 0.05 to about 0.5 gram per liter of electrolyte solution, from about 0.1 to about 0.3 gram per liter of electrolyte solution being most satisfactory in the usual case. More addition agent may be utilized but it is, in general, uneconomic to do so and fully satisfactory results are obtained in practically all cases with the preferred range set out hereinabove.

It will be understood that the addition agents

utilized should be soluble in the electrolyte solution at least to such an extent as to fall within the general range as set out hereinabove. In general, the solubility of the addition agents in the electrolyte solutions decreases with the increase of carbon atoms in the fatty acid acyl or alkyl chain of the addition agents and, therefore, lower concentrations of such addition agents may be used. Conversely, higher concentrations, generally speaking, of those addition agents should be used where the number of carbon atoms in the fatty acid acyl or alkyl chain is around 8 or 10 carbon atoms. The addition agents which are preferably employed, as indicated hereinabove, are those derived from fatty acids containing from 10 to 16 carbon atoms and of particular utility are those prepared from fatty acids containing predominantly 12 to 14 carbon atoms, the lauric acid derivatives being especially useful.

Table II sets forth various examples of plating baths with which the addition agents of the present invention may be used effectively to prevent or inhibit pitting. It will be understood that these examples are merely illustrative and are not to be taken as limitative of my invention, it being understood that, in general, the novel teachings of my invention may be utilized in connection with plating baths wherein the addition agents are soluble in the electrolyte solutions to the extent necessary to accomplish the desired results, and wherein said addition agents are not hydrolyzed or otherwise decomposed or modified to an extent sufficient to interfere with their functioning. In general, the addition agents are particularly effective in aqueous acidic electroplating baths wherein the pH of the bath is of the order of about 2 to about 6.

Table II

In each bath 0.1–0.5 gram/liter or 0.01–0.07 oz./gal. of lauric acid mono-ester of diethylene glycol sulphoacetate, sodium salt.

Nickel (white)	Conc., oz./gal.	Nickel (white)	Conc., oz./gal.
$NiSO_4.6-7H_2O$	30–40	$NiCl_2.6H_2O$	30–40
$NiCl_2.6H_2O$	8	H_3BO_3	5
H_3BO_3	5		
Temp. 100–150° F.		Temp. 70–150° F.	
pH=4.0–5.5		pH=4.0–5.5	
Cathode C. D. 5–75 amp./sq. ft.		Cathode C. D. 5–150 amp./ft.^{2}	

Nickel (bright)	Conc., oz./gal.	Cobalt	Conc., oz./gal.
$NiSO_4.6-7H_2O$	30–40	$CoSO_4.7H_2O$	30–40
$NiCl_2.6H_2O$	8	$CoCl_2.6H_2O$	8
H_3BO_3	5	H_3BO_3	5
$C_6H_5-SO_2NH_2$	0.3	$(NH_4)_2SO_4$	0.2
$ZnSO_4.7H_2O$	0.1		
Temp. 100–150° F.		Temp. 70–120° F.	
pH=3.5–5.5		pH=3.5–5.5	
Cathode C. D. 15–75 amp./ft.^{2}		Cathode C. D. 20–200 amp./ft.^{2}	

Nickel-cobalt (bright)	Conc., oz./gal.	Zinc	Conc., oz./gal.
$NiSO_4.6-7H_2O$	32	$ZnSO_4.7H_2O$	30–40
$CoSO_4.7H_2O$	8	$Zn(C_2H_3O_2)_2$	4
$NiCl_2.6H_2O$	6	$Al_2(SO_4)_3$	2
H_3BO_3	5		
HCHO	0.15		
Temp. 100–150° F.		Temp. 100–150° F.	
pH=4.0–5.5		pH=4.0–5.5	
Cathode C. D. 5–100 amp./ft.^{2}		Cathode C. D. 10–50 amp./ft.^{2}	

Iron	Conc., oz./gal.	Copper	Conc., oz./gal.
$FeCl_2$	40	$CuSO_4.5H_2O$	30–40
$CaCl_2.6H_2O$	20	$Cu(C_2H_3O_2)_2$	4
Temp. 100–150° F.		Temp. 70–150° F.	
pH=3.5–5.0		pH=3.0–5.0	
Cathode C. D. 10–100 amp./ft.^{2}		Cathode C. D. 10–50 amp./ft.^{2}	

While, in the examples listed hereinabove in Table II, I have disclosed the use of the sodium salt of the lauric acid mono-ester of diethylene glycol sulphoacetate as the addition agent, it will be understood that others of the addition agents which I have disclosed may be substituted therefor without in any manner departing from the spirit and teachings of my invention.

It will be understood that, from time to time, more addition agent should be added to replenish that which is lost by "drag-out" or which may possibly be changed, in some manner or other, during the electrodeposition process.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. In a process of electrodepositing metals, the step which comprises electrolyzing an aqueous acid solution of a salt of the metal to be deposited and a minor proportion of a soluble sulphoacetate of a water-soluble aliphatic polyhydric alcohol partially esterified with a fatty acid containing from 12 to 14 carbon atoms, the metal to be deposited being selected from the group consisting of nickel, cobalt, iron, zinc, cadmium, copper, and antimony.

2. In a process for electrodepositing metals, the step which comprises electrolyzing an aqueous acid solution of a salt of the metal to be deposited and a minor proportion of a soluble sulphoacetate of a member selected from the group consisting of glycerin and glycols, the glycerin and glycols being partially esterified with fatty acids containing predominantly from 12 to 14 carbon atoms, the metal to be deposited being selected from the group consisting of nickel, cobalt, iron, zinc, cadmium, copper, and antimony.

3. In a process for electrodepositing metals, the step which comprises electrolyzing an aqueous acid solution of a salt of the metal to be deposited and a minor proportion of a soluble sulphoacetate of a mono-ester of a water-soluble glycol with a fatty acid containing from 12 to 14 carbon atoms, the metal to be deposited being selected from the group consisting of nickel, cobalt, iron, zinc, cadmium, copper, and antimony.

4. In a process of electrodepositing nickel, the step which comprises electrolyzing an aqueous acid nickel solution containing a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, said aqueous solution also containing a minor proportion of a soluble aliphatic sulpho-mono-carboxylic acid ester of a water-soluble aliphatic polyhydric alcohol partially esterified with a fatty acid containing from 8 to 18 carbon atoms, the sulpho-mono-carboxylic acid radical containing not more than 6 carbon atoms.

5. In a process of electrodepositing nickel, the step which comprises electrolyzing an aqueous acid nickel solution containing a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, said aqueous solution also containing a minor proportion of the lauric acid mono-ester of diethylene glycol sulphoacetate.

6. In a process of electrodepositing metals, the

step which comprises electrolyzing an aqueous acid solution of a salt of the metal to be deposited, said solution containing from about 0.1 to about 0.5 gram per liter of a soluble sulphoacetate of a member selected from the group consisting of glycerin and glycols partially esterified with fatty acids containing from 8 to 18 carbon atoms, the metal to be deposited being selected from the group consisting of nickel, cobalt, iron, zinc, cadmium, copper, and antimony.

7. In a process of electrodepositing metals, the step which comprises electrolyzing an aqueous acid solution of a salt of the metal to be deposited, said solution containing from about 0.1 to about 0.5 gram per liter of a soluble sulphoacetate of a member selected from the group consisting of glycerin and glycols partially esterified with fatty acids comprising predominantly lauric acid, the metal to be deposited being selected from the group consisting of nickel, cobalt, iron, zinc, cadmium, copper, and antimony.

8. In a process of electrodepositing metals, the step which comprises electrolyzing an aqueous acid solution of a salt of the metal to be deposited and from about 0.1 to about 0.5 gram per liter of a mono-sulphoacetate of a monoglyceride of a mixture of fatty acids comprising predominantly lauric acid, the metal to be deposited being selected from the group consisting of nickel, cobalt, iron, zinc, cadmium, copper, and antimony.

9. A bath for the electrodeposition of metals comprising an aqueous acid solution of a compound of a metal to be deposited by electrolysis and a minor proportion of a soluble sulphoacetate of a water-soluble aliphatic polyhydric alcohol partially esterified with a mixture of fatty acids containing predominantly 12 carbon atoms, the metal to be deposited being selected from the group consisting of nickel, cobalt, iron, zinc, cadmium, copper, and antimony.

10. A bath for the electrodeposition of metals comprising an aqueous acid solution of a compound of a metal to be deposited by electrolysis and from about 0.1 to about 0.5 gram per liter of a mono-sulphoacetate of a water-soluble aliphatic polyhydric alcohol partially esterified with a fatty acid containing from 12 to 14 carbon atoms, the metal to be deposited being selected from the group consisting of nickel, cobalt, iron, zinc, cadmium, copper, and antimony.

11. A bath for the electrodeposition of nickel comprising an aqueous acid solution of a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, and a minor proportion of a soluble aliphatic sulpho-fatty acid ester of a water-soluble aliphatic polyhydric alcohol partially esterified with a fatty acid containing from 8 to 18 carbon atoms, the sulpho-fatty acid radical containing from 2 to 6 carbon atoms.

12. A bath for the electrodeposition of nickel comprising an aqueous acid solution of a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, and a minor proportion of the lauric acid mono-ester of a sulphoacetate of a member selected from the group consisting of glycerin and glycols.

13. A bath for the electrodeposition of nickel comprising an aqueous acid solution of a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, and a minor proportion of a mono-sulphoacetate of a lauric acid mono-ester of a glycol.

14. In a process of electrodepositing nickel to obtain a bright or lustrous deposit, the step which comprises electrolyzing an aqueous acid nickel solution containing a metal salt selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, said aqueous solution also containing minor proportions of an aryl sulphonic acid brightener and a soluble sulphoacetate of a water-soluble aliphatic polyhydric alcohol partially esterified with a fatty acid containing from 12 to 14 carbon atoms.

15. In a process of electrodepositing nickel to obtain a bright or lustrous deposit, the step which comprises electrolyzing an aqueous acid nickel solution containing a metal salt selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, said aqueous solution also containing minor proportions of the lauric acid mono-ester of diethylene glycol sulphoacetate and a brightener in the form of a compound soluble in the solution and containing the group $—SO_2.N=$.

16. A bath for the electrodeposition of nickel in the form of a bright or lustrous deposit, comprising an aqueous acid solution of a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, and minor proportions of an aryl sulphonic acid brightener and a soluble sulphoacetate of a member selected from the group consisting of glycerin and glycols, partially esterified with fatty acids containing from 8 to 18 carbon atoms.

17. A bath for the electrodeposition of nickel in the form of a bright or lustrous deposit, comprising an aqueous acid solution of a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, and minor proportions of the lauric acid mono-ester of diethylene glycol sulphoacetate and a brightener in the form of an aromatic compound soluble in the solution and containing the group $—SO_2.N=$.

HENRY BROWN.