

UNITED STATES PATENT OFFICE

2,389,135

ELECTRODEPOSITION OF METALS

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

No Drawing. Application February 21, 1941,
Serial No. 379,950

17 Claims. (Cl. 204—45)

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 electro-plating 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 electro-deposition 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 $-\text{SO}_2\text{N}-$. 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, aliphatic sulphonocarboxylic acid esters of aliphatic alcohols containing from 8 to 18 carbon atoms, the sulphonocarboxylic acid radical containing from 2 to 4 carbon atoms. Illustrative addition agents whose use falls within the scope of my present inven-

tion are, for example, sulpho-acetates of octyl alcohol, nonyl alcohol, decyl alcohol, undecyl alcohol, lauryl alcohol, tridecyl alcohol, myristyl alcohol, cetyl alcohol, stearyl alcohol, oleyl alcohol, ricinoleyl alcohol, palmitoleyl alcohol, or mixtures of such alcohols. Of particular utility are the sulpho-acetates of coconut oil mixed fatty alcohols containing predominantly lauryl alcohol or special fractions derived from coconut oil mixed fatty alcohols which are particularly high in their lauryl alcohol content. The aliphatic straight chain alcohols are particularly desired although, in certain cases, branched chain alcohol sulphoacetates may be used such as those derived from 2-n-butyl octanol-1, 2-butyl tetradecanol-1, and the like, although the results obtained are not so satisfactory. Instead of sulphoacetates, sulphopropionates, sulphobutyrate, and, in general, esters of aliphatic sulpho-monocarboxylic acids, particularly sulpho-fatty acids, containing from 2 to 4 carbon atoms with all-

tion 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 alcohol 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 alcohol chain is around 8 or 10 carbon atoms. The addition agents which are preferably employed are those derived from alcohols containing from 10 to 16 carbon atoms and of particular utility are those prepared from alcohols containing predominantly 12 to 14 carbon atoms, the lauryl alcohol derivatives being especially useful.

Table I lists several addition agents which may be employed in accordance with my invention and in the concentrations which are, in general, preferred:

Table I

Anion	Cation	Conc., grams/ liter
$\text{CH}_3-(\text{CH}_2)_9-\text{CH}_2-\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{S O}_r$ (Decyl sulphoacetate)	H ⁺ , Na ⁺ or metal of bath being used.	0.2-0.5
$\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{S O}_r$ (Lauryl sulphoacetate)	do	0.1-0.5
$\text{CH}_3-(\text{CH}_2)_{13}-\text{CH}_2-\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{S O}_r$ (Myristyl sulphoacetate)	do	0.1-0.5
$\text{CH}_3-(\text{CH}_2)_n-\text{CH}_2-\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_2-\text{S O}_r$ (Higher fatty alcohol sulphoacetates) where n=10-16 (or mixtures)	do	0.05-0.5
$\text{CH}_3-(\text{CH}_2)_{11}-\text{CH}_2-\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-(\text{CH}_2)_2-\text{S O}_r$ (Lauryl sulphopropionate)	do	0.1-0.5
$\text{CH}_3-(\text{CH}_2)_{13}-\text{CH}_2-\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-(\text{CH}_2)_2-\text{S O}_r$ (Myristyl sulphopropionate)	do	0.05-0.5
$\text{CH}_3-(\text{CH}_2)_n-\text{CH}_2-\text{O}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-(\text{CH}_2)_2-\text{S O}_r$ (Higher fatty alcohol sulphopropionates) where n=8-16 (or mixtures)	do	0.05-0.5

phatic alcohols containing from 8 to 18 carbon atoms, such as those mentioned hereinabove, may be employed. The sulphoacetates or the like 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.

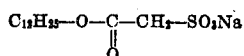
The addition agents are employed in concentrations of the general order of about 0.05 to about 0.5 gram per liter of electrolyte solution, from about 0.1 to about 0.3 gram per liter of electrolyte solution being most satisfactory in the usual case. More addition agent may be utilized but it is, in general, 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 solu-

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



Nickel (white)	Conc., oz./gal.	Nickel (white)	Conc., oz./gal.
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	30-40	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	30-40
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	8	H_3BO_3	5
H_3BO_3	5	Temp. 100-150° F.....	
Temp. 100-150° F.....		pH=4.0-5.5.....	
pH=4.0-5.5.....		Cathode C. D. 5-75.....	
Cathode C. D. 5-75.....		amp./sq. ft.	
Nickel (bright)	Conc., oz./gal.	Cobalt	Conc., oz./gal.
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	30-40	$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	30-40
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	8	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	8
H_3BO_3	5	H_3BO_3	5
$\text{C}_2\text{H}_5-\text{SO}_2\text{NH}_2$	0.3	$(\text{NH}_4)_2\text{SO}_4$	0.2
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	0.1	Temp. 70-120° F.....	
Temp. 100-150° F.....		pH=3.5-5.5.....	
pH=4.0-5.5.....		Cathode C. D. 20-200.....	
Cathode C. D. 15-75.....		amp./ft. ²	
Nickel-cobalt (bright)	Conc., oz./gal.	Zinc	Conc., oz./gal.
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	32	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	30-40
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	8	$\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$	4
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	6	$\text{Al}_2(\text{SO}_4)_3$	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. 10-50.....	
Cathode C. D. 5-100.....		amp./ft. ²	
Iron	Conc., oz./gal.	Copper	Conc., oz./gal.
FeCl_3	40	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	30-40
$\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	20	$\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$	4
Temp. 100-150° F.....		Temp. 70-150° F.....	
pH=3.5-5.0.....		pH=3.0-5.0.....	
Cathode C. D. 10-100.....		Cathode C. D. 10-50.....	
amp./ft. ²		amp./ft. ²	

While, in the examples listed hereinabove in Table II, I have disclosed the use of the sodium salt of lauryl 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 sulfo-fatty acid ester of an aliphatic monohydric alcohol containing from 8 to 18 carbon atoms, said sulfo-fatty acid containing from 2 to 4 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 sulfo-fatty

acid ester of a mixture of alcohols containing predominantly from 12 to 14 carbon atoms, the sulfo-fatty acid radical containing from 2 to 4 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 sulfo-acetate of a mixture of monohydric alcohols 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.

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 lauryl sulfo-acetate.

5. 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 sulfo-acetate of an aliphatic straight chain alcohol 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.

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 sulfo-acetate of an aliphatic straight chain monohydric alcohol 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.

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 sulfo-acetate of an aliphatic monohydric alcohol 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.

8. 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 soluble, aliphatic sulfo-mono-carboxylic acid ester of an aliphatic monohydric alcohol containing from 12 to 14 carbon atoms, the sulfo-carboxylic acid radical containing from 2 to 4 carbon atoms, 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 sulfo-acetate of an aliphatic monohydric alcohol 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.

10. 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 sulfo-fatty acid

ester of an aliphatic straight chain alcohol containing from 12 to 14 carbon atoms, the sulpho-fatty acid radical containing from 2 to 4 carbon atoms.

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 from about 0.1 to about 0.5 gram per liter of a sulpho-fatty acid ester of an aliphatic straight chain alcohol containing largely lauryl alcohol, the sulpho-fatty acid radical containing from 2 to 4 carbon atoms.

12. A bath for the electrodeposition of nickel comprising an acid aqueous solution of a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, and a minor proportion of a sulphoacetate of an aliphatic straight chain monohydric alcohol containing from 12 to 14 carbon atoms.

13. 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 material 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 sulpho-fatty acid ester of an alcohol containing from 8 to 18 carbon atoms, the sulpho-fatty acid radical containing from 2 to 4 carbon atoms.

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 material selected from the group consisting of nickel sulphate, nickel chlo-

ride, and mixtures thereof, said aqueous solution also containing minor proportions of an aryl sulphonic acid brightener and lauryl sulphoacetate.

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 material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, said aqueous solution also containing minor proportions of lauryl sulphoacetate and a brightener in the form of a compound soluble in the solution and containing the group $-\text{SO}_2\text{N}=\text{}$.

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 a soluble sulpho-fatty acid ester of an aliphatic straight chain alcohol containing from 8 to 18 carbon atoms, the sulpho-fatty acid radical containing from 2 to 4 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 a sulphoacetate of an aliphatic straight chain monohydric alcohol containing from 12 to 14 carbon atoms, and a brightener, said brightener comprising a compound soluble in the solution and containing the group $-\text{SO}_2\text{N}=\text{}$.

HENRY BROWN.