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ELECTRODEPOSITION OF NICKEL

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4 Claims. (Cl. 204—49)

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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, for example, saccharin, 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

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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 paths 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, sulphuric acid esters or sulphates of water-soluble polyhydric alcohols partially etherified with aliphatic alcohols, particularly fatty alcohols, containing from 8 to 18 carbon atoms whereas in copending application Serial No. 393,662, application May 15, 1941, now Patent 2,389,181, the compounds used as addition agents are aliphatic alkyl ether sulfonates.

Various of the addition agents utilized in accordance with the present invention may be represented by the formula

$$(R—O)_v—X—(O—SO_3M)_w$$

where R is an alkyl radical containing from 8 to 18 carbon atoms, M is a cation such as hydrogen, alkali metals or a metal corresponding to that of the metal being electrodeposited, for example, nickel, X is the residue of an aliphatic polyhydric alcohol, and v and w are small whole numbers such as 1 or 2.

The polyethylene glycol alkyl ether sulphate addition agents, whose use represents a particularly preferred embodiment of my present invention, may be represented by the formula

$$R—(O—C_2H_4)_n—OSO_3M$$

where R and M are the same as in the immediately preceding formula, and n is a whole number such as 1, 2, 3, 4, or more, preferably 2 to 4.

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) $CH_3-(CH_2)_7-O-C_2H_4-OSO_2O^-$ (Octyl alcohol mono-ether of ethylene glycol sulphate)	H^+, Na^+ or metal of bath being used.	0.1–0.5
(2) $CH_3-(CH_2)_9-O-C_2H_4-OSO_2O^-$ (Decyl alcohol mono-ether of ethylene glycol sulphate)	do	0.1–0.5
(3) $CH_3-(CH_2)_{11}-O-C_2H_4-OSO_2O^-$ (Lauryl alcohol mono-ether of ethylene glycol sulphate)	do	0.1–0.5
(4) $CH_3-(CH_2)_n-O-C_2H_4-OSO_2O^-$ where n=10 to 16 (or mixtures) (Higher fatty alcohol mono-ethers of ethylene glycol sulphate)	do	0.1–0.5
(5) $CH_3-(CH_2)_7-O-CH_2-CH(OH)-OSO_2O^-$ (Octyl alcohol mono-ether of glycerol mono-sulphate)	do	0.1–0.5
(6) $CH_3-(CH_2)_{11}-O-CH_2-CH(OH)-OSO_2O^-$ (Lauryl alcohol mono-ether of glycerol mono-sulphate)	do	0.1–0.5
(7) $CH_3-(CH_2)_7-O-C_2H_4-O-C_2H_4-OSO_2O^-$ (Octyl alcohol mono-ether of diethylene glycol sulphate)	do	0.1–0.5
(8) $CH_3-(CH_2)_{11}-O-C_2H_4-(O-C_2H_4)_2-O-C_2H_4-OSO_2O^-$ (Lauryl alcohol mono-ether of tetraethylene glycol sulphate)	do	0.1–0.5

The water-soluble aliphatic polyhydric alcohols, the specific ethers of which, in the form of sulphates, comprise the addition agents of my present invention, may be selected from a large class and include, for example, glycerin; glycols such as ethylene glycol, propylene glycol, trimethylene glycol, butylene glycol, and the like; polyglycols such as diethylene glycol, triethylene glycol, tetraethylene glycol, and the like; pentaerythritol; dipentaerythritol; 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 alcohols with which the aforementioned or similar water-soluble aliphatic polyhydric alcohols are etherified may also be selected from a large group including, by way of illustration, straight chain and branched chain alcohols such as octyl alcohol, nonyl alcohol, decyl alcohol, undecyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol, oleyl alcohol, linoleyl alcohol, stearyl alcohol, ricinoleyl alcohol, and palmitoleyl alcohol, and the like; branched chain octyl, decyl, dodecyl, tetradecyl, hexadecyl and octadecyl aliphatic alcohols as, for example, 2-ethyl hexanol-1; 2-n butyl octanol-1; 2-butyl tetra-decanol-1; 7-ethyl 2-methylundecanol-4; 3,9 diethyltridecanol-6; 3-methylheptanol-2; 5,11 diethylpentadecanol-8; 5-ethylnonanol-2; 7-ethyl-2 methyltridecanol-4; 9-ethyl-5-methyltridecanol-6; 5-ethyltridecanol-8; 3-ethylheptanol-6; 3-ethyl-8-methylnonanol-6; 3-ethylundecanol-6; and 2-methylnonanol-4. I prefer particularly to use the straight chain, unsubstituted fatty alcohols containing from 8 to 12 carbon atoms. Any of the aliphatic alcohols listed hereinabove may be etherified with any of the listed polyhydric alcohols to form partial ethers, especially mono-ethers, the sulphates, particularly mono-sulphates, of which comprise the addition agents used in accordance with the present invention.

It will be understood that the sulphuric acid or sulphate radical is linked to the remainder of the molecule of the addition agent through an hydroxy group of the aliphatic polyhydric alcohol radical. As indicated above, the molecule of the addition agent may contain one or more aliphatic or fatty alcohol radicals and one or more sulphate groups. Of especial utility are the sulphates of glycerin and glycol partial ethers of decyl and lauryl alcohols or coconut oil mixed fatty alcohols or special fractions particularly high in content of decyl or lauryl alcohols.

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 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 alkyl chain is around 8 or 10 carbon atoms.

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 mono-lauryl ether of ethylene glycol mono-sulphate, 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./ft.^{2}		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}	

Iron	conc., oz./gal.
$FeSO_4.(NH_4)_2SO_4.6H_2O$	24–32
Temp.—Room to 160° F.	
pH=4–5	
Cathode C. D., 5–100 amp./ft.^{2}	

While, in the examples listed hereinabove in Table II, I have disclosed the use of the sodium salt of monolauryl ether of ethylene glycol monosulphate 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 nickel, the step which comprises electrolyzing an aqueous acid nickel solution consisting essentially of a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, said aqueous solution also having dissolved therein in a concentration of at least .05 gram per liter a soluble mono-sulphate of a water-soluble aliphatic polyhydric alcohol the hydrogen of at least one hydroxy group of which is replaced by an alkyl radical containing from 8 to 18 carbon atoms, the sulphate group being linked directly to an hydroxy group of the aliphatic polyhydric alcohol.

2. In a process of electrodepositing nickel, the step which comprises electrolyzing an aqueous acid nickel solution consisting essentially of a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, said aqueous solution also having dissolved therein a monolauryl ether of a glycol mono-sulphate in a concentration of at least .05 gram per liter.

3. A bath for the electrodeposition of nickel consisting essentially of an aqueous acid solution of a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, said solution also having dissolved therein in a concentration of at least .05 gram per liter a soluble sulphate of a water-soluble aliphatic polyhydric alcohol the hydrogen of at least

one hydroxy group of which is replaced by an alkyl radical containing from 8 to 18 carbon atoms, the sulphate group being linked directly to an hydroxy group of the aliphatic polyhydric alcohol.

4. A bath for the electrodeposition of nickel consisting essentially of an aqueous acid solution of a material selected from the group consisting of nickel sulphate, nickel chloride, and mixtures thereof, said solution also having dissolved therein in a concentration of at least .05 gram per liter a monolauryl ether of a glycol mono-sulphate.

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