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ELECTRODEPOSITION OF METALS

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This invention relates to electrodeposition of metals.

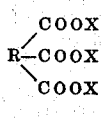
Attempts have been made to prevent pitting of metal deposits obtained by electrodeposition from electroplating baths by incorporation of various types of compounds into such baths. However, in certain instances use of such compounds have proven unsatisfactory owing, for example, to poor solubility and/or stability of such adjuvants under electrolysis conditions.

An object of the invention is to provide improved metal electroplating baths and methods for electrodeposition, utilization of which result in production of pit-free, uniform deposits. The more specific aspects of the invention include improved electroplating baths—such as fluoborate, chloride and sulfate baths of metals such as copper, lead, zinc, nickel, tin and iron—containing certain anti-pitting agents which have been found to effect pit-free electrodeposits.

The invention, other objects and the advantages thereof will appear from the following description.

In accordance with the present invention, it has been found that the objectives thereof may be accomplished by incorporating in an aqueous solution containing a salt of the metal to be deposited an ester of a sulfonated aliphatic tricarboxylic acid which ester contains from 8 to 25 carbon atoms. More particularly, it has been found that the presence of a small amount of such sulfonated aliphatic tricarboxylic acid ester, preferably in the form of a salt of the ester, in aqueous electroplating solutions—such as fluoborate, chloride and sulfate solutions of metals such as copper, lead, zinc, nickel, stannous tin or ferrous iron—eliminates pitting and formation of pin holes, and results in brighter, more uniform deposits of the electroplated metal.

The sulfonated aliphatic tricarboxylic acid esters utilized in accordance with the present invention correspond with the general formula



wherein R is an aliphatic radical containing at least one sulfo group in the form of the free sulfonic acid or a salt thereof and X is a member of the group consisting of hydrogen and a radical obtained by dehydroxylation of an alcohol, not more than two of said X substituents being hydrogen, said esters containing from 8 to 25 carbon atoms.

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The aliphatic tricarboxylic acids which may be employed in making the esters utilized in accordance with the present invention may be symmetrical or unsymmetrical, saturated or unsaturated tricarboxylic acids, as for example ethane tricarboxylic acid, propane α,α,γ tricarboxylic acid, tricarballylic acid, propane α,β,β tricarboxylic acid, propane α,α,β tricarboxylic acid, α-carboxy adipic acid, isobutane tricarboxylic acid and the unsaturated acids ethylene tricarboxylic acid, iso aconitic acid, aconitic acid, γ-butylene α,β,γ tricarboxylic acid and methyl aconitic acid. Although the above acids are typical of those which may be employed in accordance with our invention, it is apparent that other acids of the type falling within the above general formula may be used. The preferred acid for the purposes of this invention is aconitic acid.

A large variety of alcohols may be used for the formation of the esters of the present invention. Generally, any of the monohydric paraffin alcohols such as methyl and ethyl alcohol as well as the various isomers of propyl, butyl, amyl, hexyl, heptyl, octyl and higher alcohols as for example dodecyl, hexadecyl, cetyl, oleyl and stearyl may be employed. Instead of using the pure alcohols various commercial alcohols or mixtures of alcohols may be utilized such as the mixture of higher alcohols formed as a by-product in the manufacture of methanol from carbon monoxide and hydrogen. Also various polyhydric and other alcohols may be applied such as ethylene glycol, butylene glycol, diethylene glycol, and the methyl, ethyl, propyl etc. ethers of ethylene or diethylene glycol or their homologues. Typical cyclic alcohols which are also of use in the present invention include cyclohexanol, methyl cyclohexanol, benzyl alcohol, furfuryl alcohol, α-terpineol, borneol, phenol, xylenols, parabutyl phenols and other alkylated phenols or their hydrogenation products. We have found that the esters of sulfonated aconitic acid with an aliphatic alcohol such as butyl or amyl alcohol are very suitable and convenient to use in the electroplating baths of the invention and give good results.

Although we prefer to employ the tri-esters in practice, the diesters and monoesters of the above noted aliphatic tricarboxylic acids are also suitable, provided the total number of carbon atoms present in such esters ranges from 8 to 25. Further, various mixed esters may be applied. A tricarboxylic acid may be esterified with any combination of alcohols including the monohydric saturated or unsaturated alcohols, aliphatic polyhydric alcohols, their esters having at least one

remaining free hydroxyl group and other polyhydric alcohols containing at least one free hydroxyl group and in which one or more hydroxyl groups have been previously reacted with a suitable acid. Also included are acid alcohols such as ricinoleic acid containing one or more free hydroxyl groups and in the remainders of which carboxylic acid residues have been introduced.

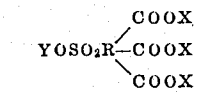
The tricarboxylic acid esters of the invention may be prepared by reaction of any of the above tricarboxylic acids with any of the above described acohols by way of the conventional methods of esterification.

One or more sulfo groups are attached to the aliphatic portion (designated by R in the general formula) of the tricarboxylic acid esters employed herein. Incorporation of such sulfo groups into the compounds of the invention may be accomplished by various sulfonation procedures. Thus, for example, saturated tricarboxylic acids may be sulfonated with strong sulfonating agents such as sulfur trioxide or fuming sulfuric acid to obtain the corresponding tricarboxylic acids containing sulfo groups, or halogen substituted saturated or unsaturated tricarboxylic acids may be treated with an alkali metal sulfite whereby a sulfo group is substituted for a halogen atom. Most desirably, however, the sulfonated aliphatic tricarboxylic acid is prepared from the corresponding unsaturated acid by addition reactions with salts of sulfurous acid. Thus, aconitic acid reacts with ammonium or alkali metal bisulfites by way of addition to form sulfonated aconitic acid which is a saturated compound also known as sulfo tricarballylic acid. The sulfonated tricarboxylic acids obtained in the above manner may then be esterified. Alternatively, the above noted sulfonation procedures may be carried out after esterification of the tricarboxylic acids. Accordingly, throughout the specification and claims, the terms "ester of a sulfonated aliphatic tricarboxylic acid" and "sulfonated aliphatic tricarboxylic acid ester" are intended to denote and include tricarboxylic acid esters which have been prepared by sulfonation either before or after esterification of the tricarboxylic acid.

The preferred compounds utilized in accordance with the invention are the salts of the esters of sulfonated aliphatic tricarboxylic acids. Throughout the specification and claims the expression "a salt of an ester" is intended to define esters which contain a basic salt-forming radical linked to a free sulfo group of the tricarboxylic acid ester. The salt-forming radicals which may be attached to the free sulfo groups include ammonium, an alkali metal, e. g. sodium and potassium, and other metals such as copper, zinc, nickel, etc. corresponding to the metal to be electroplated from the particular bath employed, and the radical of an organic base, e. g. trimethyl amine and pyridine. Formation of the above salts of the sulfonated tricarboxylic acid esters of the invention is desirable for the purpose of enhancing the solubility of such esters.

The foregoing salt-forming radicals may be incorporated into one or more of the free sulfo groups of the tricarboxylic acid esters of the invention in any suitable manner, e. g. by neutralizing such free sulfo groups with the appropriate base to form the corresponding sulfo salt of the ester. However, in the case of unsaturated tricarboxylic acid esters, sulfonation of which may be carried out by addition reactions with ammonium or alkali metal bisulfites, as indicated above, a sulfo salt may be formed directly as a result of sulfonation in this manner, e. g. sulfonation of aconitic acid ester by means of sodium bisulfite results in formation of the sodium salt of sulfonated aconitic acid ester. Instead of having sulfo salt formation take place after esterification of the aliphatic tricarboxylic acid, the sulfo salt linkage may be alternatively established first in the aliphatic tricarboxylic acid by any of the means above indicated followed by esterification of such sulfo salt of the acid.

Of the above described sulfonated tricarboxylic acid esters utilized in accordance with the invention, the preferred esters are those which may be represented by the following general formula



wherein R is an aliphatic radical, Y is a member of the group consisting of hydrogen, ammonium, the radical of an organic base, and a metal, and X is a member of the group consisting of hydrogen and a radical obtained by dehydroxylation of an aliphatic alcohol, not more than two of said X substituents being hydrogen, said esters containing from 8 to 25 carbon atoms. Specific illustrations of some of the values of R, Y and X have been mentioned above.

The following examples serve to illustrate methods of preparing the sulfonated aliphatic tricarboxylic acid esters and salts of such esters suitable for use in the invention:

Example 1.—Ethane tricarboxylic acid is dissolved in fuming sulfuric acid and the reaction is allowed to continue for a period of time under controlled temperature conditions. Excess sulfuric acid is then neutralized with barium hydroxide and the remaining solution is found to contain a mixture of mono sulfo and disulfo ethane tricarboxylic acids. This mixture is then esterified with 2-ethyl butanol in known manner to form a mixture of the corresponding esters of such acids.

Example 2.—Dry hydrochloric acid is passed into a mixture of citric acid and butyl alcohol under conditions known in the art to obtain as a reaction product tributyl citrate. The citric acid ester is then reacted with acetyl chloride in known manner to dehydrate the citric acid residue and form tributyl aconitate which latter compound is sulfonated by addition of sodium bisulfite thereto in the conventional way to produce as a reaction product a saturated compound which is the sodium salt of sulfonated tributyl aconitate, also known as tributyl sodium sulfotricarballylate.

Example 3.—Aconitic acid is reacted with sodium bisulfite under known addition reaction procedure to produce as the addition compound the saturated sodium salt of sulfonated aconitic acid, alternatively known as the sodium salt of sulfotricarballylic acid. The latter compound is esterified in known manner by treatment with amyl alcohol to produce the sodium salt of sulfonated triamyl aconitate.

In order to be suitable for the purposes of the invention it is required that the above sulfonated aliphatic tricarboxylic acid esters and salts of such esters contain from 8 to 25 carbon atoms. We have found that those esters and salts of such esters which contain more than 25 carbon atoms are too insoluble to be operable in the electroplating solutions of the invention. If the number of carbon atoms in the above compounds

in less than 8, such compounds have been found to have little effect as assistants in preventing pitting of the electrodeposited metal in accordance with the teachings of the invention.

Only a very small amount of sulfonated aliphatic tricarboxylic acid anti-pitting agents of the invention is necessary to obtain metal deposits which are uniform and pit-free. The amount of ester, salt of such ester or mixture of both which may be incorporated into metal plating solutions may vary from as little as .01 gram per liter up to saturation. No advantage is obtained in employing quantities of the tricarboxylic acid esters of the invention in excess of the amount which will dissolve in the particular metal electroplating solution utilized. In usual commercial operation when employing the preferred anti-pitting agents of the invention, namely, the alkali metal, preferably sodium salt, of sulfonated tributyl or triamyl aconitate, the amount of the more soluble butyl ester utilized may range from 0.1 to 2, preferably 0.5 to 2, grams per liter of solution, while the amount of the amyl ester applied may range from .03 to .20, preferably .05 to .15, gram per liter of solution. Of the above two compounds preferred for use in the present invention, we have found the application of the butyl ester to be more desirable.

The metal plating baths contemplated for use in the present invention may contain various other adjuvants in addition to the particular metal salt employed as an electrolyte and the small amount of sulfonated tricarboxylic acid ester incorporated therewith. Thus, free boric acid may be incorporated in the metal fluoborate electrolytes to act as a buffer in maintaining proper acidity of solution, and soluble chlorides, e. g. ammonium chloride, may be added to effect rapid anode corrosion. Small amounts of other substances such as glue, licorice and beta naphthol may also be included in the metal electroplating baths of the invention. The various adjuvants noted directly above aid to bring about formation of a strong uniform metal deposit under the most favorable operating conditions including a short electrolysis period.

In order to realize the optimum results under commercial operating conditions it may be desirable to electrolyze the metal electroplating solutions of the invention at comparatively high temperatures, for example above 100° F., thus increasing conductivity of the solution and thereby increasing the current density and efficiency at which the electroplating operation may be carried out. The ability to employ high current densities cuts down the operating time required to deposite a given thickness of metal. However, in some instances it has been found advantageous to operate at temperatures somewhat below 100° F. for best results. To obtain good anode corrosion and high efficiency it is necessary to maintain the plating solutions sufficiently acid at all times, which condition may be satisfied by having proper amounts of acidic material such as sulfuric or preferably fluoboric acid present. It is also desirable to include a buffering agent such as the above noted boric acid.

While the foregoing described principles of the invention are applicable to the electrodeposition of any suitable metal sought to be deposited from an aqueous solution of any suitable salt thereof, the present improvements are particularly directed to utilization of baths comprising aqueous solutions of fluoborates, chlorides and sulfates of suitable metals such as copper, lead, zinc, nickel, stannous tin and ferrous iron. The preferred embodiments of the invention are directed to utilization of fluoborate salt baths, especially of metals of the group including copper, lead, zinc, stannous tin and ferrous iron.

The following examples illustrate practice of the invention:

Example 4.—Copper plating

	Grams/liter
Copper fluoborate $Cu(BF_4)_2$	448
Free fluoboric acid HBF_4	8
Sodium salt of sulfonated tributyl aconitate	1
OPERATING CONDITIONS	
pH (colorimetric)	0.6
Temperature, ° F	120
Cathode current density (amps. per sq. ft.)	200
Voltage	6–8

Example 5.—Lead plating

	Grams/liter
Lead fluoborate $Pb(BF_4)_2$	370
Free fluoboric acid HBF_4	20
Glue	0.2
Sodium salt of sulfonated tributyl aconitate	1.5
OPERATING CONDITIONS	
Temperature, ° F	80
pH (colorimetric)	0.5
Cathode current density (amps. per sq. ft.)	30
Voltage	3–4

Example 6.—Lead-tin alloy plating

	Grams/liter
Total tin fluoborate	7.0
Stannous tin fluoborate	6.0
Lead fluoborate	88.0
Free fluoboric acid	40.0
Free boric acid	25.0
Sodium salt of sulfonated tributyl aconitate	2.0
OPERATING CONDITIONS	
pH	0.3
Temperature, ° F	80
Cathode current density (amps. per sq. ft.)	30
Voltage	2–3

The deposit obtained is an alloy of lead and tin containing 93% lead and 7% tin.

Example 7.—Zinc plating

	Grams/liter
Zinc fluoborate $Zn(BF_4)_2$	300
Ammonium chloride NH_4Cl	27
Ammonium fluoborate NH_4BF_4	35
Licorice	1
Sodium salt of sulfonated tributyl aconitate	.7
OPERATING CONDITIONS	
pH (colorimetric)	3.7
Temperature, ° F	130
Cathode current density (amps. per sq. ft.)	100
Voltage	3–6

Example 8.—Tin plating

	Grams/liter
Tin fluoborate $Sn(BF_4)_2$	200
Free fluoboric acid HBF_4	50
Free boric acid H_3BO_3	25
Glue	6
Beta naphthol	1
Sodium salt of sulfonated tributyl aconitate	.7

OPERATING CONDITIONS

pH (colorimetric)	0.2
Temperature, °F	80
Cathode current density (amps. per sq. ft.)	75
Voltage	3–4

Example 9.—Iron plating

	Grams/liter
Ferrous fluoborate	379
Ammonium chloride	22
Sodium salt of sulfonated tributyl aconitate	1

OPERATING CONDITIONS

Cathode current density (amps. per sq. ft.)	60
pH	3
Temperature, °F	90
Voltage	2–3

The deposits obtained by use of the foregoing baths had excellent appearance and were pit-free, fine grained and ductile.

Example 10.—Nickel plating

	Grams/liter
Nickel fluoborate $Ni(BF_4)_2$	300
Free fluoboric acid HBF_4	14
Free boric acid H_3BO_3	30
Nickel chloride $NiCl_2.6H_2O$	1.0
Sodium salt of sulfonated tributyl aconitate	1.0

OPERATING CONDITIONS

Temperature, °F	130
pH (colorimetric)	2–3.5
Cathode current density (amps. per sq. ft.)	50–250
Voltage	1–8

Example 11.—.06 gram per liter of the sodium salt of sulfonated triamyl aconitate was substituted for the sodium salt of sulfonated tributyl aconitate of Example 10.

Example 12.—Nickel plating

	Grams/liter
Nickel sulfate $NiSO_4.7H_2O$	240
Nickel chloride $NiCl_2.6H_2O$	45
Boric acid H_3BO_3	30
Sodium salt of sulfonated tributyl aconitate	1.0

OPERATING CONDITIONS

Temperature, °F	130
pH (electrometric)	4–5.5
Cathode current density (amps. per sq. ft.)	5–75
Voltage	1–4

Example 13.—0.1 gram of the sodium salt of sulfonated triamyl aconitate was substituted for the sodium salt of sulfonated tributyl aconitate of Example 12.

Example 14.—Nickel plating

	Grams/liter
Nickel Chloride $NiCl_2.6H_2O$	300
Boric acid H_3BO_3	30
Sodium salt of sulfonated tributyl aconitate	1.0

OPERATING CONDITIONS

Temperature, °F	140
pH (colorimetric)	1.5
Cathode current density (amps. per sq. ft.)	50
Voltage	3

In above Examples 10–14, the resulting nickel deposits were uniform in appearance and pit-free.

We have found that the salts of a sulfonated ester of aconitic acid and an aliphatic alcohol, which salts of the ester contain from 8 to 25 carbon atoms, particularly the sodium salt of sulfonated tributyl or triamyl aconitate, give especially good results in accordance with the invention when employed in aqueous fluoborate solutions of copper, lead, zinc, stannous tin or ferrous iron, and are of particular advantage in copper, lead or zinc fluoborate solutions, the latter three compositions and processes for electrodepositing the corresponding metal therefrom being considered to constitute the most desirable embodiments of the invention.

During electrolysis of the above electroplating baths agitation of such baths by air or by mechanical means may or may not be practiced as desired. The use of agitation generally increases the permissible current density at which sound deposits can be obtained and thus enables production of higher plating rates. Moreover, especially when operating at high temperatures, some means of agitation is preferably employed to avoid local overheating. All commercial types of anodes may be utilized with the metal electroplating baths described and claimed herein.

The tricarboxylic acid esters and salts thereof as above defined are especially effective in metal fluoborate electroplating solutions for prevention of pitting of the electrodeposited metal therefrom because of the good solubility and excellent stability of such organic compounds in metal fluoborate solutions under rigorous electrolysis conditions. The above compounds are also of value in metal fluoborate solutions for obtention of metal deposits which are fine grained and ductile. Further, the tricarboxylic acid compounds of the invention are substantially non-foaming in the electroplating baths in which they are incorporated and thus permit agitation of such baths either by air or mechanical means, whereas this advantageous expedient is not permissible in the case of the application of other anti-pitting compounds which cause foaming.

While the invention has been described particularly with respect to the use of the above sulfonated tricarboxylic acid esters and salts of such esters separately in metal electroplating solutions, such organic compounds may also be utilized in various admixtures with each other to produce the effect desired.

It will be realized by those skilled in the art that changes may be made in the metal electroplating process and in the composition of the electroplating baths of the invention without departing from the spirit thereof. The invention is therefore to be taken as limited only by the scope of the appended claims.

Reference is made to our co-pending application, Serial No. 788,685, filed Nov. 28, 1947, which claims related subject matter.

We claim:

1. The process of electrodepositing a metal which comprises electrolyzing an aqueous acid solution containing a fluoborate salt of the metal to be deposited and a minor proportion of an ester of sulfonated aconitic acid and an aliphatic alcohol, said ester containing from 8 to 25 carbon atoms.

2. The process of electrodepositing a metal which comprises electrolyzing an aqueous acid solution containing a fluoborate salt of a metal

of the group consisting of copper, lead, zinc, stannous tin and ferrous iron, and from 0.1 gram per liter up to saturation of a salt of a sulfonated ester of aconitic acid and an aliphatic alcohol, said salt of the ester containing from 8 to 25 carbon atoms.

3. The process as defined in claim 2 wherein the metal fluoborate is lead fluoborate.

4. The process as defined in claim 2 wherein the metal fluoborate is copper fluoborate.

5. The process as defined in claim 2 wherein the metal fluoborate is zinc fluoborate.

6. An electroplating bath comprising an aqueous acid solution of stannous fluoborate and 0.1 to 2 grams per liter of the sodium salt of sulfonated tributyl aconitate.

7. An electroplating bath comprising an aqueous acid solution of ferrous fluoborate and 0.1 to 2 grams per liter of the sodium salt of sulfonated tributyl aconitate.

8. An electroplating bath comprising an aqueous acid solution of the fluoborate of a metal of the group consisting of copper, lead, zinc, stannous tin and ferrous iron, and from .01 gram per liter up to saturation of a salt of a sulfonated ester of aconitic acid and an aliphatic alcohol, said salt of the ester containing from 8 to 25 carbon atoms.

9. An electroplating bath comprising an aqueous acid solution of lead fluoborate and 0.1 to 2 grams per liter of the sodium salt of sulfonated tributyl aconitate.

10. An electroplating bath comprising an aqueous acid solution of copper fluoborate and 0.1 to 2 grams per liter of the sodium salt of sulfonated tributyl aconitate.

11. An electroplating bath comprising an aqueous acid solution of zinc fluoborate and 0.1 to 2 grams per liter of the sodium salt of sulfonated tributyl aconitate.

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