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METHOD AND MEANS OF ELECTRO-DEPOSITION

Paul R. Pine, Elyria, Ohio, assignor to The Harshaw Chemical Company, Elyria, Ohio, a corporation of Ohio

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There have been known for some time several agents which as added to certain plating baths, improve the quality and character of the deposited metal. With these, limitations of one kind or another have been usual, and each metal or bath has raised its own problems. I have now found however, that a bath constituent applicable to a wide range of metals and conditions, is possible, and with production of metal deposits of excellent brightness, ductility, freedom from pin holes, and pitting.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

In accordance with the invention, I provide an electrolytic bath including an addition agent which is a sulphuric acid reaction product of such compound as a terpene, including hemiterpenes, sesquiterpenes, di-terpenes, polyterpenes, their derivatives, and related resins and oleo resins, and for conciseness, all such compounds and their synthetic analogues may be conveniently referred to as organic compounds having substantially a terpenic type nucleus. Instances of these are for example, terpenes as dipentene or racemic limonene, dextro and laevo-limonene, sylvestrene or carvestrene, alpha carene from long leaf pin oil, pinenes, as from various turpentine oils, phellandrenes, menthene, terpinolene, camphene, bornylene, etc.; hemiterpenes, as isoprene, piperylene, etc.; sesquiterpenes, as caryophyllene, cadinene from sandalwood, gurjunene as from gurjun balsam oil, santalene, cadinene as from oil of cubebs, selinene, etc.; di-terpene, as in rosin oil; polyterpenes, as rubber, balata, gutta percha, etc.; terpene alcohols, as terpineol, borneol, isoborneol, beta-terpineol as from yellow pine oil, fenchyl alcohol, geraniol, linalool, laevo-menthol, etc.; terpene aldehydes, as citral, citronellal, etc.; terpene ketones as camphor, fenchone, piperitone, racemic pipertone as from eucalyptus oil, menthone, thujone, pulegone, carvone, etc.; derivatives of terpenes, as terpin hydrate, geranic acid, camphenic acid, abietene, isoborneol acetate, borneol chloride, pinene hydrochloride, camphor oxime, isonitrosocamphor, sylvestrene nitrosate, pyrolytic products of rubber or of resins; resins generally, as kauri, Zanzibar and other African copals, Manila copal, damar, mastic, sandarac, acaroid, dragon's blood, shellac, rosin, etc.; oleoresins or balsams, as Oregon balsam from Douglas fir, Canada balsam, Peru balsam, balsam of Tolu, copaiba, gurjun, etc.; terpene-containing oils, as rosin oil, turpentine, Venice turpentine, pine oil, copaiba oil, cedarwood oil, etc. The preparation of the reaction product not being part of the present invention, is immaterial as to its detail, and it is sufficient to here say that it may have geen prepared in any known or preferred way, such as by treating the turpenoid with sulphuric acid, fuming sulphuric acid, sulphur trioxide, halogen sulphonic acids, sulphuryl halides, alkyl or aryl hydrogen sulphates, dialkyl sulphates, sulphur dioxide and air in the presence of metal oxides or salts, or any of the preceding agents in combination with a reaction promoter such as salts of iron, copper, mercury, boric acid, aluminum halides, etc.; and furthermore, the sulphuric acid reaction product may if desired, be neutralized with a base, as an alkali metal compound, such as sodium hydroxide, or the metal or a compound of the metal to be electrodeposited; and for illustration, in order to make the nature of the addition agents wholly clear, an agent may be employed which has been prepared as follows: 100 parts by weight of alpha-pinene is slowly added to 350 parts of 10 per cent oleum or fuming sulphuric acid, preferably with continuous stirring and cooling as necessary to below 60° C. The alpha-pinene being added within a period of one-half hour or less, the mixture is heated to about 85° C. for approximately 4 hours. The resulting product is soluble in water except for a very small residue, and may be employed in the plating bath as such, or may be neutralized by slow admixture of 30 per cent caustic soda solution, with cooling if necessary, to maintain the temperature below about 85° C., and the neutralization being stopped desirably just short of neutral point on the acid side. The solution, if a dry product is desired, may then be concentrated, as on a steam bath, and is available as an addition agent to metal plating baths generally, such as with copper, nickel, zinc, cadmium, tin, etc. Similarly, as another illustration, a product may be employed which has been prepared as follows: 280 parts by weight of rosin oil, de-acidified, such as from pale London oil, are slowly added to 700 parts of 20 per cent oleum, with stirring and cooling, as necessary, to maintain a temperature below about 60° C. The rosin oil being added within one-half hour or less, the mixture is heated, preferably with stirring,

for an hour or more to about 80° C. The product is water-soluble except for a very small amount of residue, and may be employed as such, or may be neutralized to a salt, as for instance by addition of a 25 per cent suspension of nickel carbonate in water. The resultant solution may be concentrated, as on a steam bath, to a soft, crumbly solid, as an addition agent for nickel plating. While as indicated, neutralization of the sulphuric acid reaction product may be stopped short of neutral point on the acid side, the addition of the neutralizing material may be carried just to the neutral point or beyond, as desired or the un-neutralized sulphuric acid reaction product may be added to the plating bath and the pH of the bath may be adjusted to any desired value by known methods.

The amount of the control agent or addition agent added to the electro-deposition bath may vary somewhat with circumstances and requirements in view, ranging for instance from about 0.01–2 oz. per gallon. Amounts thereabove are not necessary in general. Either acid or alkaline baths may be thus treated, and such operation is advantageous with various metals in wide range, as copper, nickel, zinc, cadmium, tin, etc.

As readily understood also, the ester salts of any of the terpenoids, as designated, may be employed, some being more conveniently commercially attainable than others. In general, sulphuric acid reaction products of such compounds as dipentene, pinene, oil of turpentine, caryophellene, abietene, rosin, gum damar, acid free rosin oil, etc., are particularly available conveniently.

As examples, there may be noted:

	Oz. per gal.
I. $ZnSO_4$	32–48
$ZnCl_2$	3–12
Sodium acetate	2– 8
Boric acid	2– 6
Sulphuric acid reaction product of terpenoid	4

Sulphuric acid is added to a concentration of 10 per cent.

The current density may be 10–100 amp. per square foot, and the temperature 30–35° C.

	Oz. per gal.
II. $NiSO_4$	20
$NiCl_2$	3
H_3BO_3	4.4
Sulphuric acid reaction product of terpenoid	6

$NiCO_3$ is added to a pH of 2.5 to 3.

The temperature may be 40–45° C., and the current density 10–30 amp. per square foot.

	Oz. per gal.
III. CdO	½–10
NaCN	2 –22
Na_2CO_3	2
Salt of sulphuric acid reaction product of terpenoid	.01– 4

Operating this bath at room temperature up to 35° C., a current density of 15–50 amp. per square foot yields excellent results, with clear, mirror-like deposits and smooth surface.

	Oz. per gal.
IV. $CdSO_4$	3 –24
$CdCl_2$	2 –12
H_3BO_3	2 – 8
Salt of sulphuric acid reaction product of terpenoid	.01– 8

The pH may be 3–5, and operation may be carried on at room temperature and with current density of 10–30 amp. per square foot, with excellent results.

	Oz. per gal.
V. $NiSO_4$	5 –45
$NiCl_2$	2 – 8
H_3BO_3	3 – 5.5
Salt of sulphuric acid reaction product of terpenoid	.01–12

The pH may be 1.0–6.5, and cathode current density 5–100 amp. per square foot.

	Oz. per gal.
VI. $NiSO_4$	12 –24
$NiCl_2$	2 – 6
H_3BO_3	2 – 5.5
Salt of sulphuric acid reaction product of terpenoid	.01– 8

Operation may be carried on at room temperature, and with pH of 1.0–6.5, and cathode current density 5–25 amp. per square foot.

	Oz. per gal.
VII. $CuSO_4$	20 –33
H_2SO_4	6 –12
Salt of sulphuric acid reaction product of terpenoid	.01– 4

The temperature may be 35–45° C., and a current density of 10–150 amp. per square foot may be employed.

	Oz. per gal.
VIII. CuCn	2 – 8.5
NaCn	3 –16
Na_2CO_3	2
Na_2SO_3	⅛– 1½
Salt of sulphuric acid reaction product of terpenoid	.01– 3

The current density may be 10–45 amp. per square foot.

	Oz. per gal.
IX. $ZnSO_4$	30 –50
$ZnCl_2$	3 – 8
H_2BO_3	2 – 6
Salt of sulphuric acid reaction product of terpenoid	.01–12
$NaC_2H_3O_2$	3 –10

	Oz. per gal.
X. $SnSO_4$	3 –10
H_2SO_4	4 –18
$NiSO_4$	.01– .5
NaF	.01– .2
Salt of sulphuric acid reaction product of terpenoid	.01– 8

Operation may be at room temperature and with current density of 5–60 amp. per square foot.

The invention is characterized by a wide-spread versatility of application irrespective of the bath reaction or character, and with suitable conditions, high deposition rates may be carried on without difficulty, and with attainment of attractively smooth, bright metal surfaces, and excellent metal texture.

This application is a continuation-in-part of my prior application Serial No. 695,328, filed October 26th, 1933.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:—

1. An electro-depositing bath, comprising a

solution of a compound of a metal to be deposited by electrolysis, and a sulphuric acid reaction product of an organic compound having substantially a terpenic type nucleus, said reaction product having been pre-formed.

2. An electro-depositing bath, comprising a solution of a compound of a metal to be deposited by electrolysis, and a sulphuric acid reaction product of dipentene, said reaction product having been pre-formed.

3. An electro-depositing bath, comprising a solution of a compound of a metal to be deposited by electrolysis, and a sulphuric acid reaction product of pinene, said reaction product having been pre-formed.

4. An electro-depositing bath, comprising a solution of a compound of nickel to be deposited by electrolysis, and a sulphuric acid reaction product of an organic compound having substantially a terpenic type nucleus, said reaction product having been pre-formed.

5. An electro-depositing bath, comprising a solution of a compound of nickel to be deposited by electrolysis, and a sulphuric acid reaction product of dipentene, said reaction product having been pre-formed.

6. An electro-depositing bath, comprising a solution of a compound of nickel to be deposited by electrolysis, and a sulphuric acid reaction product of pinene, said reaction product having been pre-formed.

7. A process of electro-deposition, which comprises electro-depositing a metal from a solution of a compound of the metal, there being added to such solution a sulphuric acid reaction product of an organic compound having substantially a terpenic type nucleus.

8. A process of electro-deposition, which comprises electro-depositing a metal from a solution of a compound of the metal, there being added to such solution a sulphuric acid reaction product of dipentene.

9. A process of electro-deposition, which comprises electro-depositing a metal from a solution of a compound of the metal, there being added to such solution a sulphuric acid reaction product of pinene.

10. A process of electro-deposition, which comprises electro-depositing nickel from a solution of a compound of the nickel, there being added a sulphuric acid reaction product of an organic compound having substantially a terpenic type nucleus.

11. A process of electro-deposition, which comprises electro-depositing nickel from a solution of a compound of the nickel, there being added a sulphuric acid reaction product of dipentene.

12. A process of electro-deposition, which comprises electro-depositing nickel from a solution of a compound of the nickel, there being added a sulphuric acid reaction product of pinene.

PAUL R. PINE.