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PROCESS AND MEANS FOR DEPOSITING METALS ELECTROLYTICALLY

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This invention relates to electro-deposition, and more particularly electro-deposition of metals, and it is among the objects of the invention to provide processes and means for electrolytically depositing metals with a maximum freedom from critical factors and operating handicaps.

It is a common experience that while the addition of gum tragacanth, cadmium chloride, cobalt chloride, etc., in small amounts to a high pH nickel bath gives bright deposits, these deposits are exceedingly brittle, will not receive a chromium plate without peeling, nor can they be deposited in thicknesses over two and one-half ten thousandths of an inch without peeling. On the other hand, in accordance with my invention, deposits of any thickness can be obtained at high current density and of great ductility and adherence and with a mirror finish, if plated upon a polished surface, and furthermore chromium can be plated directly upon this plate without further buffing. Applications to other metals will also be described, as well as other objects and advantages.

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.

I have found that if the metal salt of the acid produced by treating an oleoresin, its distillation products, or its derivatives, with sulphuric acid at suitable temperatures, depending upon the individual compound treated, be incorporated in an electrolytic bath for deposition of metals, freedom from pitting may be had, and a surprisingly smooth, dense, ductile thick deposit can be produced, with a great range of current density and temperature conditions. While the method of producing the sulphuric acid treated material is not a part of this invention, and such products however they be made may be used, by way of illustration I will indicate a method which yields a suitable material in the case of an industrial pine oil so that anyone skilled in the art may readily understand the nature of such addition agent. Thus, 100 g. of pine tar distillate, commercially known as "retene oil", is mixed with 233 g. of 100% sulphuric acid and thoroughly stirred while being maintained at a temperature between 80 and 90° C. When the oil is substantially solubilized by the sulphuric acid, the material is cooled, any unreacted or tarry products separated by suitable means, and the solution converted into the metal salt by treatment with a metal carbonate, hydroxide, or other suitable compounds. An alternative procedure is to add the product obtained from the sulphuric acid treatment directly to the plating bath with subsequent adjustment of the bath by addition of a basic material. I have found that under suitable conditions of treatment with sulphuric acid, the following, for instance, yield acid valuable as addition agents in electroplating; oleoresins, as obtained from the tree itself, turpentine, rosin oil, de-acidified rosin oil, balsam, copaiba balsam, colophony, abietic acid, abietene, pine tar, pine tar oil, dipentenes, compounds from distillation of pine tars including the so-called retene oil, terpineol, fenchyl alcohol, retene oil wax, camphor, iso-borneol, Gurjan balsam oil, Venice turpentine, Cade oil, African copaiba balsam, cedar oil, gum dammar, fossil gums, etc.

In the case of nickel plating, for instance, I have found that the amount of the addition or control agent added may range from a very small amount, say 1/100 oz. per gal. as a lower limit if only to prevent pitting, and as the upper limit an amount such that the bath will not become too viscous. In other words, the amount of the addition agent added is not critical. Depending upon the metal being deposited, the bath may be either acid or alkaline. In the latter case, I find it advisable to add ammonium salts to prevent precipitation of part of the addition agent. Other materials similar to ammonia, or derivatives of ammonia, may be employed for this purpose. The addition agent will operate with a wide range of metals, including tin, cadmium, zinc, copper, silver, etc. The control agent may be in the form of a salt of a particular metal which is to be electrodeposited, or as an alkali or other soluble salt compatible with the other anions in the bath. Whether the salts of the metal which is being electrodeposited or other soluble salts of the addition agent be employed is not material as long as the metal in the addition agent is higher in the electromotive series than the metal to be deposited.

In the case of nickel, these addition agents when added to a modified form of the well-known "Watts bath", as indicated in Example I, produce an extremely ductile plate with a mirror-like finish, providing it is plated upon a polished surface, while even if plated upon an unpolished surface, the tendency is that increasing thickness of deposit yields a brighter and brighter plate. It is readily possible to obtain deposits of .005 inch and more, and in fact any thickness of plate desired and, in general, the quality of the plate improves with the thickness deposited. This addition agent, therefore, produces a pit-free, ductile, bright and heavy deposit of nickel, upon which chromium can be plated directly in adherent form, a feat which so far as I am aware has thus been accomplished for the first time.

Furthermore, the current density is not particularly critical and may be employed at a rate as high as 80 amp. per square foot without injuring the deposit, whereas without this addition agent the maximum current density permissible under like operating conditions is approximately 45 amp. per square foot.

In the case of copper, the addition agent produces an extremely fine-grained plate of very soft copper with a sheen and tendency toward brightness, which may be very readily buffed to a mirror-like finish. In the case of tin, a very fine-grained, adherent deposit is obtained with a sheen. In other words, this addition agent acts to improve the characteristics of plating solutions in general.

As examples, the following may be noted:

I.	$NiSO_4.6H_2O$	6 to 60 oz. per gallon.
	$NiCl_2.7H_2O$	0 to 12 oz. per gallon.
	H_3BO_3	0 to 6 oz. per gallon.
	Addition agent	Lower limit, .01 oz. per gal. Upper limit determined only by the limit of viscosity permissible for commercial operation.
	Current density	1 to 100 amp. per sq. ft.
	Temperature	20° to 75° C.
II.	$NiSO_4.6H_2O$	26 oz. per gal.
	$NiCl_2\ 7H_2O$	4 oz. per gal.
	H_3BO_3	4½ oz. per gal.
	Addition agent (crude).	8 oz. per gal. (contains nickel sulphate crude).
	Current density	35 to 45 amp. per sq. ft.
	Temperature	35° to 45° C.
	pH	3 to 6.2.
	A higher pH requires the presence of ammonium ion or similar peptizing agent to prevent precipitation of components of the bath.	
III.	$CuSO_4$	5 to 45 oz. per gal.
	H_2SO_4	1 to 16 oz. per gal.
	Addition agent	No limit except viscosity as above noted.
IV.	CuCN	1 to 12 oz. per gal.
	NaCN	1.5 to 16 oz. per gal.
	Addition agent	.01 to 6 oz. per gal.
	Na_2CO_3	3 oz. minimum per gal.
	Na_2SO_3	½ to 3 oz. per gal.
V.	$SnSO_4$	1 to 16 oz. per gal.
	H_2SO_4	1 to 18 oz. per gal.
	Addition agent	1 to 6 oz. per gal.
	Glue	1 to 3 oz. per gal.
	$NiSO_4$	0 to 2 oz. per gal.
	Current density	20 amp. per sq. ft.
VI.	Sodium stannate	10 to 14 oz. per gal.
	NaOH	1 to 1.5 oz. per gal.
	Sodium acetate	2 to 5 oz. per gal.
	H_2O_2	½ oz. per gal.
	Addition agent	1 to 10 oz. per gal.
VII.	Cadmium oxide	½ to 10 oz. per gal.
	NaCN	2 to 22 oz. per gal.
	NaOH	½ to 6 oz. per gal.
	Addition agent	.01 to 2 oz. per gal.
VIII.	$CdSO_4$	1 to 16 oz. per gal.
	$CdCl_2$	1 to 6 oz. per gal.
	$Al_2(SO_4)_3$	1 to 12 oz. per gal.
	Addition agent	Minimum 1—no upper limit.
IX.	$ZnSO_4$	2 to 60 oz. per gal.
	$ZnCl_2$	½ to 10 oz. per gal.
	$Al_2(SO_4)_3$	1 to 12 oz. per gal.
	Sodium acetate	1 to 12 oz. per gal.
	Addition agent	1 minimum—no upper limit.
X.	$Zn(CN)_2$	½ to 10 oz. per gal.
	NaCN	½ to 16 oz. per gal.
	NaOH	½ to 3 oz. per gal.
	Addition agent	1 to 4 oz. per gal.

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-deposition bath, comprising a solution providing ions of the metal to be deposited by electrolysis and a sulphuric acid reaction product of a material selected from the group consisting of oleoresins and natural resins and their distillation products, said reaction product being pre-formed outside the bath.

2. An electro-deposition bath, comprising a solution providing ions of the metal to be deposited by electrolysis and a sulphuric acid reaction product of an oleoresin, said reaction product being pre-formed outside the bath.

3. An electro-deposition bath, comprising a solution providing ions of the metal to be deposited by electrolysis and a sulphuric acid reaction product of a distillate from an oleoresin, said reaction product being pre-formed outside the bath.

4. An electro-deposition bath, comprising a solution providing ions of the metal to be deposited by electrolysis and a sulphuric acid reaction product of a distillate from a natural resin, said reaction product being pre-formed outside the bath.

5. An electro-deposition bath, comprising a solution providing ions of the metal to be deposited by electrolysis and a sulphuric acid reaction product of rosin oil, said reaction product being pre-formed outside the bath.

6. An electro-deposition bath, comprising a solution providing ions of nickel to be deposited by electrolysis and a sulphuric acid reaction product of a material selected from the group consisting of oleoresins and natural resins and their distillation products, said reaction product being pre-formed outside the bath.

7. An electro-deposition bath, comprising a solution providing ions of nickel to be deposited by electrolysis and a sulphuric acid reaction product of an oleoresin, said reaction product being pre-formed outside the bath.

8. An electro-deposition bath, comprising a solution providing ions of nickel to be deposited by electrolysis and a sulphuric acid reaction product of a distillate from an oleoresin, said reaction product being pre-formed outside the bath.

9. An electro-deposition bath, comprising a solution providing ions of nickel to be deposited by electrolysis and a sulphuric acid reaction product of a distillate from a natural resin, said reaction product being pre-formed outside the bath.

10. An electro-deposition bath, comprising a solution providing ions of nickel to be deposited by electrolysis and a sulphuric acid reaction product of rosin oil, said reaction product being pre-formed outside the bath.

11. As a new article of manufacture, an addition agent for a plating bath comprising a sulphuric acid reaction product of a material selected from the group consisting of oleoresins and natural resins and their distillation products and their derivatives, said reaction product being pre-formed outside the bath.

12. As a new article of manufacture, an addition agent for a plating bath comprising a sulphuric acid reaction product of an oleoresin, said reaction product being pre-formed outside the bath.

13. As a new article of manufacture, an addi-

tion agent for a plating bath comprising a sulphuric acid reaction product of a distillate from an oleoresin, said reaction product being pre-formed outside the bath.

14. As a new article of manufacture, an addition agent for a plating bath comprising a sulphuric acid reaction product of a distillate from a natural resin, said reaction product being pre-formed outside the bath.

15. As a new article of manufacture, an addition agent for a plating bath comprising a sulphuric acid reaction product of rosin oil, said reaction product being pre-formed outside the bath.

16. A process of electro-deposition, which comprises electrolyzing a metal from a solution containing the same and a sulphuric acid reaction product of a material selected from the group consisting of oleoresins and natural resins and their distillation products, said reaction product being pre-formed outside the bath.

17. A process of electro-deposition, which comprises electrolyzing a metal from a solution containing the same and a sulphuric acid reaction product of an oleoresin, said reaction product being pre-formed outside the bath.

18. A process of electro-deposition, which comprises electrolyzing a metal from a solution containing the same and a sulphuric acid reaction product of a distillate from an oleoresin, said reaction product being pre-formed outside the bath.

19. A process of electro-deposition, which comprises electrolyzing a metal from a solution containing the same and a sulphuric acid reaction product of a distillate from a natural resin, said reaction product being pre-formed outside the bath.

20. A process of electro-deposition, which comprises electrolyzing a metal from a solution containing the same and a sulphuric acid reaction product of rosin oil, said reaction product being pre-formed outside the bath.

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