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ELECTRODEPOSITION OF NICKEL

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This invention relates to nickel plating and more especially to processes of and solutions for nickel plating characterized by the presence in the plating solution of one or more organic compounds effective to improve the character of the deposit.

Already nickel electroplating solutions of the Watts type containing coumarin or one of certain substitution products thereof have been developed, and to a considerable extent, commercialized. The present invention has to do with the discovery that if such solutions contain a small amount of formaldehyde, they can be used for a longer period of time before it becomes necessary to purify the solution. It is common practice in the operation of nickel plating solutions containing organic compounds to purify the solution occasionally by adding activated carbon, agitating the solution so as to contact all parts of the liquid therewith and then filter. The activated carbon thus adsorbs impurities from the solution and removes them. This procedure is naturally not made use of any more often than necessary since it requires time and effort and usually removes material which is desirable in the solution and must be replaced. Accordingly, it is very desirable to prolong the interval between purification treatments as much as possible. In accordance with the present invention it has been found possible to prolong the interval between purifications of solutions containing coumarin and certain substitution products thereof to give periods of trouble-free operation several times as long as would otherwise be obtainable. The action of formaldehyde seems to be specific to this type of addition agent. While it is not known with certainty what the action is, it has been fairly well established that there exists in solutions of this type, after long periods of operation small quantities of conversion products of coumarin or of such coumarin substitution product. It is believed that the lactone ring opens up giving under reducing conditions orthohydroxy phenyl propionic acid and derivatives thereof which not only do not have the beneficial effects of the parent material but are harmful when the concentration becomes substantial.

It has been found that formaldehyde renders these conversion products harmless, or at least much less harmful, to an extent which increases the length of trouble-free periods of operation between filtrations. The periods of trouble-free operation vary accordingly to circumstances, depending upon the kind of metallic and other impurities which find their way into the solutions and the conditions of operation.

By making this orthohydroxy phenyl propionic acid synthetically outside of the plating bath, and then adding it to the bath, we have secured identical results to those secured by continued operation of a coumarin bath.

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When orthohydroxy phenol propionic acid is present, it tends to give undesirable characteristics to the nickel electrodeposit. The deposit, with increasing amounts of the acid, becomes slate gray rather than semi-bright particularly in the lower cathode current density areas (at e. g., about 15 amperes per square foot or less). Further, the stress in the deposit increases with increasing concentration of the acid, and again the effect is greatest in the low current density areas; when sufficient of the acid is present, the stress becomes sufficiently high to cause cracking and crazing of the electrodeposit.

We have found, however, that when a relatively large amount of orthohydroxy phenyl propionic acid is present, good plates with normal stress can be secured if formaldehyde is added to the bath. Thus, without addition of formaldehyde to the bath, the presence of $\frac{1}{2}$ -1 gram per liter of the acid will cause slate grayness in the low current density areas while with formaldehyde, 4 grams per liter or more of the acid (presumably tied up in a complex with the formaldehyde) can be tolerated without harmful effects in the electrodeposit.

In the coumarin bath not treated with formaldehyde, gradual formation of the acid during operation has necessitated treatment of the bath after 1-2 months but with formaldehyde, the treatment period can be delayed considerably.

We have found that the orthohydroxy phenyl propionic acid concentration can be allowed to rise to an equilibrium value which varies somewhat in the range 3-5 grams per liter of the acid. Under laboratory conditions a test solution has been kept going by the use of formaldehyde for nearly a year without purification. In the operation of commercial solutions, treatment every few months is to be expected. Nevertheless, the period between treatments can be increased, frequently doubled or better, by the use of formaldehyde. The amount of formaldehyde required varies considerably with the type of installation since a large and variable proportion is lost by evaporation. In our laboratory tank we have found $\frac{1}{4}$ - $\frac{1}{2}$ cc. per day of 40% formaldehyde solution per liter of solution is adequate. In plant tests, it appears that smaller amounts are required, in some cases as little as .03 cc. per day per liter of solution being satisfactory.

We are not certain of the action of the formaldehyde in the bath. In some tests, added formaldehyde evaporated less rapidly from baths containing the orthohydroxy propionic acid than from those which did not have the acid present. We believe that the orthohydroxy phenyl propionic acid and formaldehyde form a resin or complex.

The solutions by means of which the present invention may be realized are those which contain

nickel sulfate, a mixture of nickel sulfate and nickel chloride, nickel fluoborate, nickel sulfamate, or a mixture of nickel fluoroborate and nickel sulfate as the principal or sole source of nickel ions and which are operated at a pH value

the conversion product is formed, it reacts with formaldehyde and is prevented from producing gray deposit.

Preferred solutions and conditions of operation are as follows:

	Sulfate Bath, g./l.	Sulfate-Chloride, g./l.	Fluoborate Bath, g./l.	Sulfamate Bath, g./l.
NiSO ₄ ·6H ₂ O	160-400	160-300	0-120	
NiCl ₂ ·6H ₂ O		30-75		
Ni(BF ₄) ₂			40-120	
Ni(SO ₃ NH ₂) ₂				100-200
H ₂ BO ₃	15-40	15-40	15-40	15-40
Wetting Agent ¹	0.1-1	0.1-1	0.1-1	0.1-1
Auxiliary Brightener	0-10			
Coumarin ²	.05-.5	.05-.5	.05-.5	.05-.5
Formaldehyde	1-5	1-5	1-5	1-5
Current Density	15-60	15-60	15-60	15-60
Temperature (° F.)	120-160	120-160	120-160	120-160
pH	3.5-5	3.5-5	3.5-5	3.5-5
H ₂ O	remainder	remainder	remainder	remainder

¹ The preferred wetting agent is sodium lauryl sulfate although other wetting agents reported in the literature may be used. A preferred class of wetting agents includes the sulfates of normal primary aliphatic alcohols having from 8 to 18 carbon atoms. These are desirable but may be omitted.

² The substitution products of coumarin listed below or any of them may be substituted for coumarin in the first column of this table.

on the acid side. The pH may be and preferably is adjusted to lower values by sulfuric acid or hydrochloric acid or both and to higher values by nickel carbonate or nickel hydroxide or both. It is preferable that the solution contain a buffer such as boric acid, formic acid, sodium formate or the like. It is also desirable that the solution contain an anti-pit agent. These are of the type of compounds called wetting agents since they produce lowering of the surface tension. It is generally thought that the lowering of the surface tension frees the hydrogen bubbles which otherwise frequently adhere to the cathode and prevent deposition of metal. It is not always necessary to use an anti-pit agent but it is customary to do so since any plating bath is otherwise likely to be subject to pitting at times.

The amount of formaldehyde to be added at any one time depends upon the manner of its use. If a concentration of formaldehyde is maintained at all times, it preferably should be kept at from 0.05 to 0.5 gram per liter. It is also possible to utilize formaldehyde only after the buildup of orthohydroxy phenyl propionic acid has become great enough to cause grayness of deposit in areas of low cathode current density. We have found that a satisfactory "dosage" of formaldehyde for a solution beginning to give areas of slate grayness in the deposit is from 0.1 to 0.3 gram per liter. More can be used without causing any undesirable results up to say 1.5 grams per liter. As the amount of formaldehyde is increased further, the deposit tends to become harder and the scratch filling character of the bath decreases. It can thus be seen that the solution may be operated with a constant concentration of formaldehyde so that as soon as

Coumarin may be used in concentration of from 0.05 to 0.50 gram per liter of solution or to complete saturation, but we prefer to use a concentration of from 0.2 to 0.25 gram per liter. Substitution products of coumarin which may be used instead of coumarin are numerous. For example, we may use those wherein the substituents are alkyl or acyl groups not exceeding four carbon atoms, halogen or carboxy groups. Coumarin sulfonic acids are unsatisfactory since they produce deposits which exhibit poor power to cover scratch marks and poor buffability as compared with coumarin. We prefer to use coumarin or some of the other derivatives of coumarin which give results substantially equivalent to those secured by the use of coumarin itself. Cyano coumarins also fail to give the excellent scratch hiding power and buffability and we prefer not to use them. The substituent group or groups may be in the 3, 4, 5, 6, 7 or 8 position, these being the positions occupied by hydrogen atoms in coumarin. Mixtures of the above indicated preferred addition agents can be used with good results. Any derivative of coumarin may be expected to be at least fairly satisfactory if it is soluble in the bath to the extent of at least about .05 gram per liter and if the substituent group or groups are inert in the solution or approximately so, for example, nickel or cobalt salts of coumarin carboxylic acids. Concentration of addition agents dissolved in the solutions tabulated above may vary within the limits of solubility but preferably should not exceed one and one-half grams per liter. Examples of substituted coumarins and the preferred concentration ranges thereof in such solutions operating in a pH range from 3.3 to 5.0 are as follows:

	Preferred pH Range	Conc. of Addition Agent, g./l.		
		Optimum pH Range	Limit	Preferred
Coumarin	3.3-5.0	3.5-4.5	.05-.5	.25
4 Methyl coumarin	3.3-5.0	3.5-4.5	.1-Sat. (1.0)	.9
6 Chloro coumarin	3.3-5.0	3.5-4.5	.06-Sat. (.25)	.2
3 Acetyl coumarin	3.3-5.0	3.5-4.5	.1-Sat. (.7)	.3
Coumarin-3-carboxylic acid	3.3-5.0	3.5-4.5	0.4-Sat. (1.8)	.7
4,8-Dimethyl coumarin	3.3-5.0	3.5-4.5	.15-Sat. (.6)	.4
3-Chloro coumarin	3.3-5.0	3.5-4.5	0.05-Sat. (.4)	.2
3-Methyl coumarin	3.3-5.0	3.5-4.5		

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The following specific examples will serve to illustrate the invention:

Example I

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	g--	300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	g--	40
H_3BO_3	g--	40
Sodium lauryl sulfate	g--	0.5
Coumarin	g--	0.25
Formaldehyde	g--	0.25
H_2O to make one liter.		
pH		3.5
Temperature	°F--	140
C. D.	A. S. F--	50

This solution by comparative tests gives a deposit which buffs very easily and which fills base metal imperfections to a large extent. The deposit is semi-bright. This solution was run for more than 300 days without treatment with activated carbon and without producing grayness in the low current density areas. Ingredient concentrations were maintained within the optimum ranges stated above. A similar solution but containing no formaldehyde began to produce deposits having slate gray areas in regions of low cathode current density (15 amps./sq. ft. and lower), after running only 20 days

Additional examples illustrative of the invention are tabulated below:

Composition No.	1	2	3	4	5	6	7	8	9	10	11	12
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	g./l. 300	320	340	300	300	300	---	50	---	---	---	---
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	g./l. 40	20	---	30	---	40	---	---	---	---	---	120
$\text{Ni}(\text{BF}_4)_2$	g./l. ---	---	---	---	---	---	100	100	---	---	---	---
$\text{Ni}(\text{SO}_3\text{NH}_2)_2$	g./l. ---	---	---	---	---	---	---	---	150	200	150	---
H_3BO_3	g./l. 40	25	30	40	20	40	20	---	15	30	40	40
Sodium Lauryl Sulfate	g./l. 0.5	0.5	0.5	0.4	0.6	0.5	0.2	---	0.2	0.3	0.25	0.2
Formaldehyde	g./l. 0.25	0.25	0.1	0.4	0.3	0.3	0.4	0.25	0.3	0.2	0.1	0.7
Coumarin	g./l. ---	---	---	---	---	---	0.25	0.25	---	0.3	---	---
3-chloro coumarin	g./l. 0.3	---	---	---	---	---	---	---	0.3	---	---	---
4-methyl coumarin	g./l. ---	0.9	---	---	---	---	---	---	---	---	---	---
4,8-dimethyl coumarin	g./l. ---	---	0.4	---	---	---	---	---	---	---	---	---
3-acetyl coumarin	g./l. ---	---	---	3	---	---	---	---	---	---	0.3	---
6-Chloro coumarin	g./l. ---	---	---	---	2	---	---	---	---	---	---	---
Coumarin-3-carboxylic acid	g./l. ---	---	---	---	---	7	---	---	---	---	---	0.6
H_2O to make 1 liter												
Current Density, A. S. F.	50	50	40	40	30	25	40	---	35	40	30	30
Temperature	160	140	120	130	140	120	130	140	130	140	150	140
pH	3.5	3.5	3.5	4.0	3.5	3.7	3.5	3.6	4.0	4.0	3.5	3.5

Having thus described our invention, what we claim is:

1. A nickel plating process comprising the steps of establishing a nickel plating solution essentially consisting of an aqueous, acid solution of nickel material supplying nickel ions and an addition agent dissolved in said solution and capable of imparting to deposits produced therein improved smoothness and buffability, said solution essentially consisting of a composition of the class consisting of aqueous solutions of nickel sulfate, aqueous solutions of nickel sulfate and nickel chloride, aqueous solutions of nickel fluoborate, aqueous solutions of nickel fluoborate and nickel sulfate and aqueous solutions of nickel sulfamate and said addition agent being selected from the class consisting of coumarin and its substitution products wherein a substituent of the class consisting of alkyl radicals containing not more than four carbon atoms, acyl radicals containing not more than four carbon atoms, halogen and carboxyl groups replaces a hydrogen atom of the coumarin, such addition agent being dissolved in said solution in concentration from 0.05 gram per liter to saturation, passing current through said solution from an anode to a cathode, adding formaldehyde to said solution and thereafter passing current from said anode to said cathode through the resulting solution,

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the amount of formaldehyde so added being in the range from 0.05 to 1.5 grams per liter.

2. A nickel plating process according to claim 1 wherein said addition agent is coumarin.

3. A nickel plating process according to claim 1 wherein said addition agent is 3-chloro-coumarin.

4. A nickel plating solution as defined in claim 1 wherein said nickel material is:

	Grams per liter
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	160 to 300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	30 to 150

5. A nickel plating solution as defined in claim 1 wherein said nickel material is:

	Grams per liter
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	160 to 300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	30 to 150

20. and said addition agent is coumarin, in concentration from 0.05 to 0.50 gram per liter and the pH of said solution is from 3.0 to 5.0.

6. A nickel plating solution as defined in claim 1 wherein said nickel material is:

	Grams per liter
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	160 to 300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	30 to 150

and said addition agent is 3-chloro-coumarin in

concentration from 0.1 to 0.4 gram per liter and the pH of said solution is from 3.0 to 5.0.

7. A nickel plating solution essentially consisting of an aqueous acid solution of nickel material supplying nickel ions and an addition agent dissolved in said solution and capable of imparting to deposits produced therein improved smoothness and buffability, said solution essentially consisting of a composition of the class consisting of aqueous solutions of nickel sulfate, aqueous solutions of nickel sulfate and nickel chloride, aqueous solutions of nickel fluoborate, aqueous solutions of nickel fluoborate and nickel sulfate and aqueous solutions of nickel sulfamate and said addition agent being selected from the class consisting of coumarin and its substitution products wherein a substituent of the class consisting of alkyl radicals containing not more than four carbon atoms, acyl radicals containing not more than 4 carbon atoms, halogen and carboxyl groups replaces a hydrogen atom of the coumarin, such addition agent being dissolved in said solution in concentration from 0.05 gram per liter to saturation, said solution also containing from 0.05 to 1.5 grams per liter of formaldehyde.

8. A nickel plating solution according to claim 7 wherein said addition agent is coumarin and

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is present to the extent of from 0.05 to 0.50 gram per liter.

9. A nickel plating solution according to claim 7 wherein said addition agent is 3-chloro coumarin and is present to the extent of from 0.05 to 0.30 gram per liter.

10. A nickel plating solution as defined in claim 7 wherein said nickel material is:

	Grams per liter
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	160 to 300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	30 to 150

11. A nickel plating solution as defined in claim 7 wherein said nickel material is:

	Grams per liter
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	160 to 300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	30 to 150

and said addition agent is coumarin, in concentration from 0.05 to 0.50 gram per liter and the pH of said solution is from 3.0 to 5.0.

12. A nickel plating solution as defined in claim 7 wherein said nickel material is:

	Grams per liter
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	160 to 300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	30 to 150

and said addition agent is 3-chloro coumarin in concentration from 0.05 to 0.30 gram per liter and the pH of said solution is from 3.0 to 5.2.

13. A nickel plating solution essentially consisting of an aqueous, acid solution of nickel material supplying nickel ions and an addition agent dissolved in said solution and capable of imparting to deposits produced therein improved smoothness and buffability, said solution essentially consisting of a composition of the class consisting of aqueous solutions of nickel sulfate, aqueous solutions of nickel sulfate and nickel chloride, aqueous solutions of nickel fluoborate, aqueous solutions of nickel fluoborate and nickel sulfate and aqueous solutions of nickel sulfamate and said addition agent being selected from the class consisting of coumarin and its

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substitution products wherein a substituent of the class consisting of alkyl radicals containing not more than four carbon atoms, acyl radicals containing not more than 4 carbon atoms, halogen and carboxyl groups replaces a hydrogen atom of the coumarin, such addition agent being dissolved in said solution in concentration from 0.05 gram per liter to saturation, said solution also containing from 0.05 to 1.5 grams per liter of formaldehyde, and 0.1 to 1.0 gram per liter of a normal primary aliphatic alcohol sulfate having from 8 to 18 carbon atoms.

14. A nickel plating solution according to claim 13 wherein said addition agent is coumarin and is present to the extent of from 0.05 to 0.50 gram per liter.

15. A nickel plating solution according to claim 13 wherein said addition agent is 3-chloro-coumarin and is present to the extent of from 0.05 to 0.30 gram per liter.

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