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ELECTROPLATING OF NICKEL

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34 Claims. (Cl. 204—49)

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My invention relates to improvements in the electrodeposition of nickel from aqueous acidic baths. It is particularly concerned with the utilization of certain addition agents for the purpose of decreasing grain size and increasing the luster of the nickel plate or deposit, and it is especially concerned with the production of electrodeposits of brilliant, highly lustrous, ductile nickel plates.

I have discovered that the grain size of electrodeposits may be decreased and the luster of the nickel deposit increased, all in an effective manner, by the utilization of certain bath-soluble organic compounds, specifically, certain aliphatic esters of unsaturated aliphatic polycarboxylic acids, the unsaturation of which acids is due solely to double bonds. Particularly satisfactory are the methyl and ethyl esters of unsaturated aliphatic polycarboxylic acids containing from 4 to 8 carbon atoms although excellent results are also obtained through the utilization of certain alkoxy alkyl esters of such unsaturated aliphatic polycarboxylic acids. The esters whose utilization is contemplated by my present invention are those wherein all of the carboxyl groups of the unsaturated aliphatic polycarboxylic acids are esterified.

The following Table I lists a number of representative esters whose use falls within the scope of my present invention. It will be understood that the solubility of such esters varies. For effective results they should be soluble in the aqueous acidic nickel plating bath to the extent of the order of at least about 0.15 gram per liter. In general, it is unnecessary to utilize the even more soluble ones of such esters in amounts greater than approximately 3 grams per liter. In all cases, it will be understood that the esters whose use is contemplated in accordance with the present invention must be soluble in the aqueous acidic nickel electroplating bath to a degree sufficient to enable such esters to exert the effect of decreasing the grain size of the electroplate of nickel and increasing the luster thereof.

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Table I

Esters of Unsaturated Dicarboxylic Acids	Conc., grams/liter
1. Dimethyl fumarate	0.2–2.0
2. Dimethyl chlorofumarate	0.2–2.0
3. Dimethyl bromofumarate	0.2–2.0
4. Di-(2-methoxy ethyl) fumarate	0.2–2.0
5. Dimethyl maleate	0.2–2.0
6. Diethyl maleate	0.2–2.0
7. Dimethyl chloromaleate	0.2–2.0
8. Di-(2-methoxy ethyl)maleate (Di-"Methyl Cellosolve" maleate)	0.2–2.0
9. Di-(2-ethoxy ethyl)maleate (Di-"Cellosolve" Maleate)	0.2–2.0
10. Dimethyl itaconate	0.2–2.0
11. Diethyl itaconate	0.2–2.0
12. Di-(2-methoxy ethyl)itaconate	0.2–2.0
13. Di-(2-(β methoxyethoxy)ethyl)itaconate	0.2–2.0
14. Dimethyl methylene malonate	0.2–2.0
15. Dimethyl glutaconate	0.2–2.0
16. Dimethyl mesaconate	0.2–2.0
17. Dimethyl citraconate	0.2–2.0
18. Dimethyl crotylidenemalonate	0.2–2.0
19. Methyl ethyl maleate	0.2–2.0
20. Methyl, 2-methoxy ethyl fumarate	0.2–2.0
21. Di-(2-ethoxy ethyl) fumarate	0.2–2.0
22. Di-(2-ethoxy ethyl)itaconate	0.2–2.0

Esters of Unsaturated Tricarboxylic Acids	Conc., grams/liter
1. Trimethyl ethylenetricarboxylate	0.2–2
2. Trimethyl α propylene, α,α,γ tricarboxylate	0.2–2
3. Trimethyl iso-aconitate (trimethyl α propylene α,γ,γ tricarboxylate)	0.2–2
4. Trimethyl aconitate (trimethyl α propylene α,β,γ tricarboxylate)	0.2–2
5. Trimethyl allenetricarboxylate	0.2–2
6. Trimethyl oxalocitraconate	0.2–2
7. Tri-(2-methoxy ethyl)aconitate	0.2–2
8. Tri-(2-methoxy ethyl)ethylenetricarboxylate	0.2–2

Esters of Unsaturated Tetracarboxylic Acids	Conc., grams/liter
1. Tetramethyl ethylene tetracarboxylate	0.2–2
2. Tetramethyl γ carboxylate aconitate	0.2–2
3. Tetramethyl α carboxylate aconitate	0.2–2
4. Tetramethyl α,γ dicarboxylate glutaconate	0.2–2

Particularly advantageous are the esters of 2-methoxy ethanol; 2-ethoxy ethanol; as, for example, di-(2-methoxy ethyl) fumarate; di-(2-methoxy ethyl)maleate; tri-(2-methoxy ethyl)

aconitate; di-(2-ethoxy ethyl)maleate; di-(2-ethoxy ethyl) fumarate; and also the methyl esters such as dimethyl maleate, dimethyl fumarate, trimethyl aconitate, and dimethyl itaconate, used either alone, or in mixtures with one another, or in conjunction with organic sulphur-containing brighteners, as described hereafter.

I have also discovered that if there is utilized in the plating bath, in conjunction with the aforesaid esters, a small proportion of a brightener of the organic sulfonic, sulfonamide or sulfonimide type, exceptionally brilliant, highly lustrous, ductile nickel plates having excellent adherence characteristics to the base metal are obtained. While it has heretofore been known to utilize brighteners of the aforesaid organic sulfonic, sulfonamide and sulfonimide types, as is disclosed in part, for example, in my prior Patents Nos. 2,191,813 and 2,466,677, it should be understood that I do not claim any invention herein the utilization of such known brighteners per se. So far as this phase of my invention is concerned, a coaction takes place in the cathode film, the exact nature of which is unknown, involving the ester of the aliphatic unsaturated polycarboxylic acid and the organic sulfur-containing brightener, which produces the unusual and highly important results which are brought about in accordance with this aspect of my invention. In this connection, it may be noted that the utilization of the esters of the aliphatic unsaturated polycarboxylic acids alone or the utilization of the organic sulfur-containing brighteners alone gives no indication of the remarkably enhanced results which occur when both types of compounds are present in the bath, particularly when utilized in their optimum concentrations. Typical examples of organic sulfur-containing brighteners which may be utilized in accordance with my present invention, in conjunction with the esters of aliphatic unsaturated polycarboxylic acids, are disclosed in my prior Patents Nos. 2,191,813 and 2,466,677 and in Table II.

Table II

Sulfur-Containing Brighteners	Optimum Conc., grams/liter
1. Benzene sulfonamide	0.1–3
2. Toluene sulfonamides (o- and p-)	0.1–2
3. o-Benzoyl sulfimide	0.1–2
4. N-Benzoyl benzene sulfonimide	0.1–1
5. p-Toluene sulfonchloramide	0.1–1
6. p-Brom benzene sulfonamide	0.1–1
7. 6-Chlor o-Benzoyl sulfimide	0.1–1
8. m-Aldehydo benzene sulfonamide	0.1–1
9. Sulfomethyl benzene sulfonamide	0.1–6
10. Benzene sulfonamide m-carboxylic amide	0.1–3
11. 7-Aldehydo o-benzoyl sulfimide	0.1–3
12. N-Acetyl benzene sulfonimide	0.1–2
13. Methoxy benzene sulfonamides	0.1–1
14. Hydroxymethyl benzene sulfonamide	0.1–2
15. Vinyl sulfonamide	4–12
16. Allyl sulfonamide	4–12
17. Benzene sulfonic acids (mono-, di-, and tri-)	1–15
18. p-Brom benzene sulfonic acid	3–6
19. Benzaldehyde sulfonic acids (o, m, p)	2–6
20. Diphenyl sulfone sulfonic acid	1–8
21. Naphthalene sulfonic acids (mono-, di-, and tri-)	1–8
22. Benzene sulfohydroxamic acid	1–5
23. p-Chlor benzene sulfonic acid	1–15
24. Diphenyl sulfonic acid	1–5
25. m-Diphenyl benzene sulfonic acid	1–4
26. 2-Chloro-5-sulfobenzaldehyde	1–5
27. m-Benzene disulfonamide	0.5–1
28. Allyl sulfonic acid	4–12

It will be understood that said sulfonic brighteners may be utilized in their acid form or in the form of salts as, for example, nickel, sodium, potassium or other salts. Especially satisfactory, for use in the practice of my present invention, are the compounds of Table II corresponding to numbers 1, 2, 3; 18, 19, 21 and 28, the latter particularly in the form of their nickel salts. Where the term sulfonic acids is used herein and in the claims, it will be understood that the salts thereof are likewise included.

The compounds of Table II produce bright and mirror-like deposits on buffed metals such as buffed brass. However, at least in the ordinary case, they do not accomplish the same results on steel polished with 180 emery or on matte (but unburnt) copper plate of 0.0003''–0.0005'' thickness but, rather generally yield plates of somewhat dull and gray appearance in these cases. The compounds of Table I, in the usual case, give a different type of plate than that produced by the compounds of Table II. The plates produced with the compounds of Table I are generally cloudy and milky on buffed or matte metal. The rate of improvement of luster of the base or basis metal is much more rapid with the compounds of Table I, per se, than with the compounds of Table II, per se. If, however, the two different types of compounds represented in Tables I and II are used together in the baths, as I have indicated above, a brilliant mirror-like deposit is obtained even over a matte surface.

In the usual case, the compounds of Table I tend to be consumed at a faster rate during the electroplating process than the compounds of Table II. The compounds of Table I, in general, have a faster rate of reduction at the nickel cathode with respect to the nickel ion, whereas the compounds of Table II, in general, have a slower rate, that is, the nickel ion is reduced preferentially in the latter case.

The aqueous nickel plating baths may be of various types but, in all cases, they are acidic in character. The preferred baths are those of the Watts' type or modifications thereof. The nickel salts may comprise nickel chloride, nickel sulfate, nickel fluoborate, nickel sulfamate, or other nickel salts or mixtures of any two or more of said nickel salts, preferably in conjunction with buffer materials as, for example, boric acid. I prefer to utilize boric acid in the bath as it is, in general, the best cathode film buffer. Other buffers of acidic character may, however, be employed as, for example, formic acid, fluoboric acid, and the like, and such may be used either in place of or in conjunction with boric acid. For optimum results, the concentration of the boric acid or its equivalent should be above 30 grams per liter, especially in baths operated at somewhat elevated temperatures. The baths may also contain various supplemental agents such as anti-pitting agents and the like. In Table III, I list preferred embodiments of bath compositions.

As I have indicated previously, the concentration of the Table I compounds in the bath may range from about 0.2 gram to about 3 grams per liter. For optimum results, a range of about 0.6 gram to 2 grams per liter usually is approximately correct. In certain, and perhaps most, cases, these concentrations are close to saturation for the particular esters utilized. Continuous filtration and the use of surface active agents to prevent pitting tend to aid in solubilizing at least to a certain extent the compounds of Table I and such procedures are, therefore, recommended in at least most cases. Where the esters of Table I which are selected for use have an appreciable vapor pressure at the temperature at which the bath is operated, suitable ventilation should be provided.

Table III

Bath No.	$NiSO_4.6H_2O$	$NiCl_2.6H_2O$	H_3BO_3	Temperature, ° C.	Optimum pH	Addition Agents
	grams/liter	*grams/liter*	*grams/liter*			
1	300	40	40	40 to 50	2.8 to 4.8	Dimethyl fumarate, 2 grams/liter.
2	300	40 to 75	40	40 to 65	2.8 to 4.8	Di(2-methoxy ethyl)maleate, 2 grams/liter plus Benzene sulfonamide, 2 to 3 grams/liter and/or o-benzoyl sulfimide, 0.1 to 2 grams/liter.
3	300	40	40	40 to 65	2.8 to 4.8	Trimethyl aconitate, 2 grams/liter.
4	300	40	40	40 to 65	2.8 to 4.8	Trimethyl ethylene tricarboxylate, 2 grams/liter plus o-benzoyl sulfimide, 0.1 to 2 grams/liter.
5	300	40	40	40 to 65	2.8 to 4.8	Tetramethyl ethylene tetracarboxylate, 2 grams/liter.
6	300	40 to 75	40	40 to 65	2.8 to 4.8	Tetramethyl ethylene tetracarboxylate, 2 grams/liter plus Benzene sulfonamide, 2 grams/liter.
7	0 to 100	0 to 40	0 to 40	40 to 65	2.8 to 5.0	Trimethyl aconitate, 2 grams/liter.
		$Ni(BF_4)_2$ 100 to 300				

The baths can be operated at temperatures ranging from about room temperature to almost boiling but, in general, the preferred temperature is in the range of about 40 degrees C. to 65 degrees C. Where the baths are operated at somewhat elevated temperatures, it will be understood that the esters of the unsaturated aliphatic polycarboxylic acids selected should be those which are stable at the bath temperatures. In general, the baths can be operated at pH values ranging from about 2 to about 5.5 but, in the ordinary case, the preferred pH values are from 3.0 to 4.8. The cathode current density ranges are quite variable, a range of about 5 to several hundred amperes per square foot being utilizable, the optimum depending upon agitation, temperature, and concentration and type of nickel salts utilized in the bath. A good working range is about 20 to about 80 amperes per square foot. Most of the compounds of Table I function optimumly at pH values of about 3.8 to 4.5 and at bath temperatures of about 45 degrees C. to 60 degrees C. Generally speaking, the lower the temperature of the bath, the higher the pH value at which the bath should be operated for obtaining optimum results.

It should be understood that while certain of the esters of Table I, for example, dimethyl fumarate, may serve best for the accomplishment of the reduction of grain size and the production of a ductile, lustrous though milky deposit when used alone, such esters are not necessarily the best ones to achieve, in conjunction with utilization of the organic sulfur-containing brighteners, the production of bright mirror-like deposits over matte metal surfaces. Thus, for example, a better conjoint effect is produced through the utilization of di-(2-methoxy ethyl) maleate in conjunction with o-benzoyl sulfimide than with dimethyl fumarate in conjunction with o-benzoyl sulfimide. Moreover, the di-(2-methoxy ethyl) maleate has the practical advantage over the dimethyl fumarate in that it is less volatile and is easier to handle in relation to odors, effects on the skin and the like.

I have also found that the presence of free 2-methoxy ethanol or 2-phenoxy ethanol or the like in the baths in concentrations of about 1 to 15 grams per liter or even higher help to brighten the medium and lower current density areas, especially when the compounds of Table II are also present with the compounds of Table I. The free 2-methoxy ethanol or similar compounds may be present in the reaction mixture resulting from the processes of preparation of the esters of such ethanol derivatives, for example, di-(2-methoxy ethyl) maleate, or they may be added as such to the baths.

It will be understood that, from time to time, it is necessary to replenish the bath to replace losses due to cathodic processes, to "drag-out," and to other causes, in order to maintain the concentrations of the added esters, etc. in operative proportions.

When the unsaturated esters (Table I) are used without the organic sulfur compounds (Table II) in the nickel baths (especially the high sulfate type), it is often advantageous to use such sequestering agents as trimethylamine α,α',α''-tricarboxylic acid, ethylene diamine tetra-acetic acid, or their salts (in concentrations up to about 3 grams per liter) for their beneficial effect in the cathode film in aiding ductilization of the high current density plate especially when the pH values are between about 3.5–5.0.

What I claim as new and desire to protect by Letters Patent of the United States is:

1. A bath for the electrodeposition of nickel comprising an aqueous acidic solution of at least one nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel fluoborate and nickel sulfamate, said bath also containing, in solution, not more than about .5% of at least one bath-soluble fully esterified aliphatic ester of an unsaturated aliphatic polycarboxylic acid, said ester being unsaturated and the unsaturation of which is due solely to double bonds in the said acid.

2. A bath for the electrodeposition of nickel comprising an aqueous acidic solution of at least one nickel salt selected from the group consisting of nickel chloride, nickel sulfate nickel fluoborate and nickel sulfamate, said bath also containing, in solution, not more than about 0.5% of at least one bath-soluble fully esterified aliphatic ester of an unsaturated aliphatic polycarboxylic acid, said polycarboxylic acid containing from 4 to 8 carbon atoms and the unsaturation of which is due solely to double bonds, and said ester being unsaturated and the unsaturation of said ester being due solely to double bonds in the said acid.

3. A bath in accordance with claim 2, wherein said ester is di-(2-methoxy ethyl) maleate.

4. A bath in accordance with claim 2, wherein said ester is di-(2-methoxy ethyl) fumarate.

5. A bath in accordance with claim 2, wherein said ester is di-(2-methoxy ethyl) itaconate.

6. A bath in accordance with claim 2, wherein said ester is di-(2-ethoxy ethyl) maleate.

7. A bath in accordance with claim 2, wherein said ester is di-(2-ethoxy ethyl) fumarate.

8. A bath in accordance with claim 2, wherein said ester is di-(2-ethoxy ethyl) itaconate.

9. A bath in accordance with claim 2, wherein said ester is at least one selected from the group

consisting of dimethyl esters of maleic acid, fumaric acid, and itaconic acid.

10. A bath for the electrodeposition of nickel comprising an aqueous acidic solution of at least one nickel salt selected from the group consisting of nickel sulfate, nickel chloride, nickel fluoborate and nickel sulfamate, said bath also containing, in solution, not more than about .5% at least one bath-soluble fully esterified aliphatic ester of an unsaturated aliphatic polycarboxylic acid, said ester being unsaturated and the unsaturation of which is due solely to double bonds in said acid, and of at least one brightener selected from the group consisting of organic sulfonamides, sulfonimides, and sulfonic acids.

11. A bath for the electrodeposition of nickel comprising an aqueous acidic solution of at least one nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel fluoborate and nickel sulfamate, said bath also containing, in solution, not more than about 0.5% of at least one bath-soluble fully esterified aliphatic ester of an unsaturated aliphatic polycarboxylic acid, said polycarboxylic acid containing from 4 to 8 carbon atoms and the unsaturation of which is due solely to double bonds, said ester being unsaturated and the unsaturation of said ester being due solely to double bonds in the said acid, and not more than about 0.5% of at least one brightener selected from the group consisting of organic sulfonamides, sulfonimides, and sulfonic acids.

12. A bath in accordance with claim 11, wherein said ester is di-(2-methoxy ethyl) maleate.

13. A bath in accordance with claim 11, wherein said ester is di-(2-methoxy ethyl) fumarate.

14. A bath in accordance with claim 11, wherein said ester is di-(2-methoxy ethyl) itaconate.

15. A bath in accordance with claim 11, wherein said ester is di-(2-ethoxy ethyl) maleate.

16. A bath in accordance with claim 11, wherein said ester is di-(2-ethoxy ethyl) fumarate.

17. A bath in accordance with claim 11, wherein said ester is di-(2-ethoxy ethyl) itaconate.

18. A bath in accordance with claim 11, wherein said ester is at least one selected from the group consisting of dimethyl esters of maleic acid, fumaric acid, and itaconic acid.

19. A bath in accordance with claim 2, wherein said ester is trimethyl aconitate.

20. A bath in accordance with claim 11, wherein said ester is trimethyl aconitate.

21. A bath in accordance with claim 12, wherein the brightener is benzene sulfonamide.

22. A bath in accordance with claim 14, wherein the brightener is p-toluene sulfonamide.

23. A bath in accordance with claim 18, wherein the brightener is o-benzoyl sulfimide.

24. A bath in accordance with claim 11, wherein said ester is di-(2-methoxy ethyl) maleate, said bath also containing a small percentage of 2-methoxyethanol.

25. A bath in accordance with claim 11, wherein said ester is di-(2-methoxy ethyl) itaconate, said bath also containing a small percentage of 2-methoxyethanol.

26. A method of electrodepositing nickel to obtain a fine-grained deposit which comprises electrolyzing an aqueous acidic bath containing at least one nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel fluoborate and nickel sulfamate, said bath also containing, in solution, not more than about .5% of at least one bath-soluble fully esterified aliphatic ester of an unsaturated aliphatic polycarboxylic acid, said ester being unsaturated and the unsaturation of which is due solely to double bonds in said acid.

27. A method of electrodepositing nickel to obtain a fine-grained deposit which comprises electrolyzing an aqueous acidic bath containing at least one nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel fluoborate and nickel sulfamate, said bath also containing, in solution, not more than about 0.5% of at least one bath-soluble fully esterified aliphatic ester of an unsaturated aliphatic polycarboxylic acid, said polycarboxylic acid containing from 4 to 8 carbon atoms and the unsaturation of which is due solely to double bonds, said ester being unsaturated and the unsaturation of said ester being due solely to double bonds in the said acid.

28. A method of electrodepositing nickel to obtain brilliant, lustrous, ductile nickel deposits which comprises electrolyzing an aqueous acidic bath containing at least one nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel fluoborate and nickel sulfamate, said bath also containing, in solution, not more than about .5% of at least one bath-soluble fully esterified aliphatic ester of an unsaturated aliphatic polycarboxylic acid, said ester being unsaturated and the unsaturation of which is due solely to double bonds in said acid, and of at least one brightener selected from the group consisting of organic sulfonamides, sulfonimides, and sulfonic acids.

29. A method of electrodepositing nickel to obtain brilliant, lustrous, ductile nickel deposits which comprises electrolyzing an aqueous acidic bath containing at least one nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel fluoborate and nickel sulfamate, said bath also containing, in solution, not more than about 0.5% of at least one bath-soluble fully esterified aliphatic ester of an unsaturated aliphatic polycarboxylic acid, said polycarboxylic acid containing from 4 to 8 carbon atoms and the unsaturation of which is due solely to double bonds, said ester being unsaturated and the unsaturation of said ester being due solely to double bonds in the said acid, and not more than about 0.5% of at least one brightener selected from the group consisting of organic sulfonamides, sulfonimides, and sulfonic acids.

30. A composition for addition to an aqueous acidic bath containing at least one nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel fluoborate and nickel sulfamate, to produce in said bath a concentration of the ingredients of said composition not more than about 0.5%, said composition consisting of at least one brightener selected from the group consisting of organic sulfonamides, sulfonimides, and sulfonic acids, and, in addition, a bath-soluble fully esterified aliphatic ester of an unsaturated aliphatic polycarboxylic acid, said ester being unsaturated and the unsaturation of which is due solely to double bonds in said acid.

31. An additive for addition to aqueous acidic solutions of at least one nickel salt selected from the group consisting of nickel chloride, nickel sulfate, nickel fluoborate and nickel sulfamate, to produce in said bath a concentration of the ingredients of said composition not more than about 0.5%, said composition consisting of at least one brightener selected from the group consisting of organic sulfonamides, sulfonimides, and

sulfonic acids, and, in addition, a bath-soluble fully esterified aliphatic ester of an unsaturated aliphatic polycarboxylic acid, said polycarboxylic acid containing from 4 to 8 carbon atoms and the unsaturation of which is due solely to double bonds and said ester being unsaturated and the unsaturation of said ester being due solely to double bonds in the said acid.

32. A composition in accordance with claim 31, wherein said ester is at least one selected from the group consisting of dimethyl esters of maleic acid, fumaric acid, and itaconic acid.

33. A composition in accordance with claim 31, wherein said ester is a di-(2-methoxy ethyl) ester of a dicarboxylic acid.

34. A composition in accordance with claim 31, wherein said ester is trimethyl aconitate.

References Cited in the file of this patent

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