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BRIGHT NICKEL PLATING

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This invention relates to bright nickel plating. The invention is based on my discovery that water-soluble olefinic alcohols and polyalcohols having four or more carbon atoms in their molecules, when incorporated as addition agents in a nickel electroplating bath in combination with various non-olefinic sulfo-oxygen compounds of the sulfonic acid type, are very effective for promoting the formation of bright ductile nickel electrodeposits. I have found that all water-soluble olefinic alcohols containing four or more carbon atoms per molecule are effective brighteners when used in combination with a sulfo-oxygen compound of the character contemplated by the invention; and I have found that in all instances the use of the non-olefinic sulfo-oxygen compound in combination with the olefinic alcohol leads to improved results as compared with use of the olefinic alcohol alone.

A preferred process according to this invention for producing bright nickel deposits comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt, in which there is dissolved from about 0.05 to 1.5 grams per liter of a water-soluble olefinic alcohol having at least four carbon atoms in its molecule, together with about 1/2 to about 75 grams per liter of a water-soluble non-olefinic sulfo-oxygen compound of the group consisting of mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, alkali metal, ammonium, magnesium and nickel salts of said acids, and mononuclear aromatic sulfonamides and imides.

While any water-soluble olefinic alcohol having at least four carbon atoms in its molecule can be employed with success in the above-defined process for producing bright nickel deposits, I have had particular success in the production of ductile bright electrodeposits when using an olefinic alcohol selected from the group consisting of 2-butene-1,4-diol, glycerol-alpha-allylether, 4-methyl-4-pentene-2-ol, 3-methyl-1-butene-3-ol, and monovinylcarbitol. Compounds in this group are particularly effective brighteners in nickel electroplating baths, and lead to the formation of bright nickel deposits of adequate ductility, when dissolved in the bath in an amount ranging from 0.1 to 0.5 gram per liter, and when used in combination with about 1 to about 15 grams per liter of a sulfo-oxygen compound of the character specified.

Brightener additions according to this invention have of course been used successfully in the standard Watts nickel electroplating bath. However, these brightener additions are also effective in all other acid nickel electroplating baths, and the invention therefore is applicable to any nickel electrodeposition operation from an aqueous acidic solution of one or more nickel salts.

Examples of olefinic alcohols which I have used successfully in embodiments of this invention, and the preferred concentration in which they are employed, are listed in Table I below under the heading "Group A" compounds:

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TABLE I

Group A compounds

		G./l.
1.	2-butene-1,4-diol, HOCH ₂ CH=CHCH ₂ OH	0.2 to 0.5
2.	Glycerol-alpha-allylether, H ₂ C=CHCH ₂ OCH ₂ CHOHCH ₂ OH	0.3 to 0.6
3.	4-methyl-4-pentene-2-ol, CH ₃ CH(OH)CH ₂ C(CH ₃)=CH ₂	0.2 to 0.5
4.	3-methyl-1-butene-3-ol, H ₂ C=CHC(CH ₃) ₂ OH	0.1 to 0.5
5.	Monovinylcarbitol, CH ₂ =CHOCH ₂ CH ₂ OCH ₂ CH ₂ OH	0.3 to 0.5

Of the compounds listed in Table I, particularly satisfactory results have been obtained using 2-butene-1,4-diol within the concentration range shown opposite it.

The sulfo-oxygen compounds used in accordance with the invention are non-olefinic, that is, they are compounds having molecules which are free of olefinic linkages, although they may (and preferred compounds do) contain aromatic substituents. The compounds listed in Table II are examples of non-olefinic sulfo-oxygen (Group B) compounds which are used in combination with a water-soluble olefinic alcohol (Group A compound) to promote formation of brilliant and adequately ductile nickel deposits. These sulfo-oxygen compounds may be used over a wide range of concentrations (1/2 to 75 grams per liter) but preferably are used in an amount in the range from about 1 to about 15 grams per liter.

TABLE II

Group B compounds

(1) Mononuclear aromatic sulfonic acids, and alkali metal, ammonium, magnesium and nickel salts thereof.

35	Benzene monosulfonic acid, C ₆ H ₅ SO ₃ H
	Sodium benzene monosulfonate, C ₆ H ₅ SO ₃ Na
	Nickel benzene monosulfonate, (C ₆ H ₅ SO ₃) ₂ Ni
40	Sodium para-toluene monosulfonate, CH ₃ C ₆ H ₄ SO ₃ Na
	Para-chlorobenzene sulfonic acid, ClC ₆ H ₄ SO ₃ H
	Sodium para-chlorobenzene sulfonate, ClC ₆ H ₄ SO ₃ Na
	Sodium para-bromobenzene sulfonate, BrC ₆ H ₄ SO ₃ Na
	1,2 dichlorobenzene sulfonic acid, Cl ₂ C ₆ H ₃ SO ₃ H
45	1,2 or 2,5 dichlorobenzene sulfonate sodium salt, Cl ₂ C ₆ H ₃ SO ₃ Na
	Meta-benzene disulfonic acid, C ₆ H ₄ (SO ₃ H) ₂
	Sodium meta-benzene disulfonate, C ₆ H ₄ (SO ₃ Na) ₂
	Nickel meta-benzene disulfonate, C ₆ H ₄ (SO ₃) ₂ Ni
50	Ortho-sulfobenzoic acid monoammonium salt, HOCOC ₆ H ₄ SO ₃ NH ₄
	1-amino-2,5-benzene disulfonic acid, H ₂ NC ₆ H ₃ (SO ₃ H) ₂
	Ortho-aminobenzene sulfonic acid, H ₂ NC ₆ H ₄ SO ₃ H

(2) Mononuclear aromatic sulfinic acids, and alkali metal, ammonium, magnesium and nickel salts thereof.

55	Sodium benzene sulfinate, C ₆ H ₅ SO ₂ Na
	Sodium para-toluene sulfinate, CH ₃ C ₆ H ₄ SO ₂ Na

(3) Mononuclear aromatic sulfonamides and imides.

60	Benzene sulfonamide, C ₆ H ₅ SO ₂ NH ₂
	Para-toluene sulfonamide, CH ₃ C ₆ H ₄ SO ₂ NH ₂
	Ortho-benzoic sulfimide,



65	Benzyl sulfonamide, C ₆ H ₅ CH ₂ SO ₂ NH ₂
	Benzene sulphydroxamic acid, C ₆ H ₅ SO ₂ NHOH
	N,N dimethyl para-toluene sulfonamide, CH ₃ C ₆ H ₄ SO ₂ N(CH ₃) ₂
70	N,N dicarboxyethyl benzene sulfonamide, C ₆ H ₅ SO ₂ N(C ₂ H ₄ COOH) ₂

(4) Binuclear aromatic sulfonic acids and alkali metal, ammonium, magnesium, and nickel salts thereof.

2-naphthalene monosulfonic acid, $C_{10}H_7SO_3H$
 1,5 or 2,7-naphthalene disulfonic acid, $C_{10}H_6(SO_3H)_2$
 1,5 or 2,7-naphthalene disulfonic acid nickel salt,
 $C_{10}H_6(SO_3)_2Ni$
 Naphthalene trisulfonic acid, $C_{10}H_5(SO_3H)_3$
 Naphthalene trisulfonic acid trisodium salt,
 $C_{10}H_5(SO_3Na)_3$
 Diphenyl pp' disulfonic acid, $HSO_3C_6H_4-C_6H_4SO_3H$
 2-naphthol-3,6-disulfonic acid, $HOC_{10}H_5(SO_3H)_2$
 2-naphthol-3,6-disulfonic acid sodium salt,
 $HOC_{10}H_5(SO_3Na)_2$

bath composition, and operating conditions, below which maximum brilliancy is not obtained. Increase in the concentration of Group B compound beyond this minimum frequently produces more ductile nickel deposits.

Brilliant nickel electrodeposits may be obtained, in accordance with the invention, from the baths listed in Table III. These baths advantageously are operated at a pH of 3.5 and at 40 amperes per square foot, with air agitation. The baths of Table III are merely examples of the ranges of bath compositions that may be used successfully, and do not indicate any limit of bath composition which can be employed in accordance with the invention:

TABLE III

	Bath concentrations in grams per liter						
	Bath 1	Bath 2	Bath 3	Bath 4	Bath 5	Bath 6	Bath 7
Nickel sulfate, $NiSO_4 \cdot 7H_2O$ -----	240-330	330	330	330			240
Nickel chloride, $NiCl_2 \cdot 6H_2O$ -----	30-45				0-37.5	0-37.5	30
Nickel formate, $Ni(OOCH)_2 \cdot 2H_2O$ -----						210	45
Nickel fluoborate, $Ni(BF_4)_2$ -----							
Nickel sulfamate, $Ni(O_2SNH_2)_2$ -----					225		
Sodium chloride, $NaCl$ -----			29.5				
Sodium bromide, $NaBr$ -----				51.5			
Boric acid, H_3BO_3 -----	30-37.5	37.5	0-37.5	0-37.5	30	30	37.5
2-butene-1,4-diol-----	0.2-0.5	0.3	0.2	0.2	0.3	0.3	1.0
1,3,6-naphthalene trisulfonate (sodium salt)-----	1-5	4.0	4.0	4.0	2.0	2.0	2.0
Temp., ° C-----	25-60	50	50	50	50	50	80

1-naphthylamine-3,6,8-trisulfonic acid,
 $H_2N \cdot C_{10}H_4(SO_3H)_3$

(5) Heterocyclic sulfonic acids and alkali metal, ammonium, magnesium and nickel salts thereof.

Thiophene sulfonic acid, $C_4H_3S \cdot SO_3H$
 Sodium thiophene sulfonate, $C_4H_3S \cdot SO_3Na$
 2-(4-pyridyl) ethyl sulfonic acid, $C_5H_4N \cdot CH_2CH_2SO_3H$

In all cases the free sulfonic acids and their alkali metal, ammonium, magnesium, and nickel salts are the full equivalents of each other for purposes of this invention. Of the sulfo-oxygen compounds listed in Table II, I have found the sodium salt of naphthalene trisulfonic acid to be particularly satisfactory, especially when used in the concentration range from about 1 to about 15 grams per liter.

At low current density and/or high temperature the concentration of the naphthalene trisulfonic acid (or other Group B compound) should be kept rather low in order to avoid milkiness of the deposit in the low current density areas, especially if the butenediol (or other Group A compound) concentration is very low (say only 0.2 g./l.). At 0.3 g./l. of butenediol, the concentration limits for naphthalene trisulfonate are extremely wide.

When a Group B compound is used alone, only dull or whitish semibright to almost bright nickel deposits are obtained. When used in combination with an olefinic alcohol of four or more carbon atoms (Group A compound), however, the sulfo-oxygen (Group B) compounds produce brilliant nickel deposits, even on unbuffed basis surfaces. A leveling (smoothing) action also is produced in many cases when a Group A compound is used in the presence of a Group B compound.

If maximum ductility of the nickel deposits is required the concentration of Group A compounds should be kept at the minimum required to produce the desired degree of brilliancy, which is generally within the range of values given in Table I. For rapid buildup of brightness of relatively thin deposits (0.0001 to 0.0005 inch) higher concentrations of Group A brighteners (e. g. up to 1.0 or even up to a maximum of 1.5 grams per liter) may be used with advantage.

As mentioned above, the concentration range of Group B addition agents is rather wide. There is a certain minimum Group B compound concentration, depending on the concentration of the Group A compound, the

An example of a standard Watt's bath falling within the composition range given for bath 1 in Table III, which has been used with particular success in accordance with the invention, is one containing 270 g./l. $NiSO_4 \cdot 7H_2O$, 45 g./l. $NiCl_2 \cdot 6H_2O$, 37.5 g./l. boric acid, 2 g./l. naphthalene trisulfonic acid sodium salt, 0.3 g./l. 2-butene-1,4-diol, having a pH of 3.5 and operated at 50° C. and 40 amperes per square foot average current density to produce brilliant electrodeposits 0.001 inch thick. When using a standard Watt's bath containing 0.2 gram per liter of butenediol and 2.0 grams per liter of 1,3,6-naphthalene trisulfonate sodium salt, operated at 50° C. and 40 amperes per square foot, the optimum pH value is in the range from 3.0 to 5.0. At a pH of 2.5 the butenediol concentration must be increased (say, to 0.4 to 0.5 gram per liter) in order to produce a deposit of full brightness.

In order to obtain pit-free nickel deposits, it is advantageous to employ strong air or mechanical agitation of well-filtered solutions, or alternatively to use less strong agitation of a bath containing 0.05 to 0.5 g./l. of a suitable antipit or wetting agent, such as an alkyl aryl sulfonate or a sodium alcohol sulfate (e. g. 0.25 gram per liter of sodium lauryl sulfate).

I claim:

1. A process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved from about 0.05 to about 1.5 grams per liter of 2-butene-1,4-diol and from about 1/2 to about 75 grams per liter of a water-soluble sulfo-oxygen compound selected from the group consisting of mononuclear and binuclear aromatic sulfonic acids, heterocyclic sulfonic acids, mononuclear aromatic sulfinic acids, alkali metal, ammonium, magnesium and nickel salts of said acids, and mononuclear aromatic sulfonamides and imides.

2. A process according to claim 1 wherein the amount of 2-butene-1,4-diol dissolved in the solution is in the range from 0.1 to 0.5 gram per liter and the amount of said water-soluble sulfo-oxygen compound dissolved in the solution is in the range from 1 to 15 grams per liter.

3. A process for producing bright nickel deposits which comprises electrodepositing nickel from an aqueous acidic solution of at least one nickel salt in which there is dissolved from about 0.2 to about 0.5 gram per liter

of 2-butene-1,4-diol and from about 1 to about 15 grams
per liter of naphthalene trisulfonic acid sodium salt.

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