

UNITED STATES PATENT OFFICE

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ELECTRODEPOSITION OF NICKEL

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This invention relates to electrodeposition of metals, and more specifically to a process of, and solutions for use in a process of electrodepositing nickel characterized in that the resulting nickel electrodeposit is bright as it comes from the plating solution. More particularly, the present invention has to do with the discovery of cooperating addition agents suitable for use in an aqueous acid nickel plating solution.

I have now discovered that excellent bright, ductile, and smooth deposits of nickel can be produced over a wide cathode current density range by electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, if such solution also contains an effective amount of each of two cooperating addition agents, one of such addition agents being a polyalkylene amine soluble in said solution to the extent of at least 0.0001 gram per liter, and having a molecular weight from 100 to 1800 or higher; and the other of said addition agents being a cyclic, organic compound soluble in the acid nickel solution to the extent of at least 0.2 gm. per liter, and selected from the group consisting of organic compounds containing the group



should be maintained in the solution in a concentration of from 0.2 to 15.0 gm. per liter, preferably from 1 to 7 gm. per liter.

Since the two above mentioned classes of addition agents are intrinsically and functionally distinct, they will be separately described and identified.

The substances of the first addition agent class, the alkylene amines, are soluble to the extent of at least 0.0001 gm. per liter in the plating solution (for example in a solution containing 240 gm. per liter $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 37.5 gm. per liter of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and 37.5 gm. per liter of H_3BO_3 , remainder water), and are those having a molecular weight from 100 to 1800 or higher, preferably from 600 to 1800.

The general formula for the unsubstituted alkylene amine compounds is as follows:



where m is an integer from 2 to 4 inclusive, and n is an integer greater than 2, preferably 12 to 40. Not only unsubstituted alkylene amines but also alkylene amines having substituents on the nitrogen, replacing hydrogen thereon, may be utilized within the molecular weight limitations set forth above.

Examples of compounds which may be reacted with the unsubstituted alkylene amines to replace amino hydrogen and increase the molecular weight of the alkylene amine are as follows:

TABLE I

Reactant	Mols	Solvent	Temperature, Degrees C.	Time, Hours
(1) Epichlorohydrin	1-2	H_2O , Toluene	70-90	0.5-1
(2) Epichlorohydrin + Phenol (Na)	1:1	H_2O	70-90	0.5-1
(3) Benzenesulfonyl Chloride	1-2	H_2O + Alkali	25-30	1-2
(4) Styrene Oxide	1	Toluene	90-110	2-5
(5) Methyl Sulfate	1-15	H_2O , 25% NaOH	40-90	0.5-16
(6) Acrylonitrile	4-7	None	150 (final)	2-8
(7) Chloroacetic Acid	2	H_2O	100-105	3-4
(8) Dimethyl Chloroacetate	2	None	130	6

wherein the carbon atom is nuclear carbon, and in which compounds each of the remaining nuclear carbon atoms carries a group of the class consisting of hydrogen, methyl, ethyl, chlorine, bromine, CHO, and phenyl. The first mentioned agent may be referred to as the alkylene amine brightener and should be maintained in the plating solution in concentration from 0.0001 to 0.1 gm. per liter, preferably from 0.0005 to 0.05 gm. per liter, while the second mentioned addition agent, which I prefer to call a carrier or regulator,

The ratio of polyalkylene amine (e.g. tetraethylene pentamine) to reactant named above are given by way of example only. Other ratios produce good results.

From the foregoing, it will be seen that the alkylene amines of the indicated molecular weights are generally suitable, irrespective of the type of substituent and size of the molecule, within the limits of the small solubility required to make possible the small concentrations needed to bring about a high order of brightening accom-

panied by high ductility and good throwing power. The alkylene amines lower than tetraethylene pentamine are not very effective unless substituted so as to bring up the molecular weight. Numerous compounds can be used, as indicated, for increasing the molecular weight, and the substitution products are often somewhat superior to the forms of lower molecular weight. This is true even of tetraethylene pentamine, which, although a good brightener, is improved by increasing the size of the molecule.

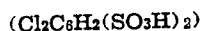
The carriers or regulators constituting the second addition agent class are soluble in the plating solution (for example, in a solution consisting of 240 grams of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 37.5 grams $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 37.5 grams of H_3BO_3 , and water to make a liter) to the extent of at least 0.2 gram per liter. These include such materials as benzene and thiophene sulfonic acids and salts thereof and halogen, methyl, ethyl, CHO, and phenyl substitution products of the foregoing, such as for example:

Carriers or regulators

1. Benzene mono-sulfonic acid ($\text{C}_6\text{H}_5\text{SO}_3\text{H}$)
2. Benzene disulfonic acids ($\text{C}_6\text{H}_4(\text{SO}_3\text{H})_2$)
3. Sodium benzene monosulfonate ($\text{C}_6\text{H}_5\text{SO}_3\text{Na}$)
4. Nickel benzene monosulfonate [$(\text{C}_6\text{H}_5\text{SO}_3)_2\text{Ni}$]
5. Monochlor benzene monosulfonic acids



6. Benzene monosulfonamide ($\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$)
7. Saccharine, sodium salt ($\text{C}_6\text{H}_4\text{SO}_2\text{CONa}$)
8. Dichloro benzene disulfonic acids



9. 2,5-dibromo benzene sulfonic acid



10. Toluene sulfonic acids ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$)
11. Benzaldehyde sulfonic acids



12. Diphenyl sulfonic acids ($\text{C}_6\text{H}_5\text{C}_6\text{H}_4\text{SO}_3\text{H}$)
13. Benzene sulfonyl chloride ($\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$)
14. Para chloro benzene sulfonamide



15. Xylene sulfonamides ($(\text{CH}_3)_2\text{C}_6\text{H}_3\text{SO}_2\text{NH}_2$)
16. Para toluene sulfonamide ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$)
17. Thiophene sulfonic acids ($\text{C}_4\text{H}_3\text{S}\cdot\text{SO}_3\text{H}$)
18. Diphenyl sulfone ($\text{C}_6\text{H}_5\text{SO}_2\text{C}_6\text{H}_5$)
19. Naphthalene-1,5-disulphonic acid
20. Sulfonated naphthalene. (Mixtures of naphthalene sulfonic acids, produced by treating naphthalene with oleum, preferably 2 parts of 20% oleum on one part of naphthalene at 160°C . for two hours)
21. Alpha naphthalene monosulfonic acid
22. Beta naphthalene mono sulfonic acid
23. O-toluene sulfonamide
24. Chloro naphthalene disulfonates

Potassium and cobalt salts are useable as well as the sodium and nickel salts indicated above.

From these examples it becomes clear that numerous single ring compounds containing the effective group can be used, whether aromatic, such as the benzene sulfonic acids or heterocyclic with aromatic characteristics, such as thiophene sulfonic acid. Various substituents on the ring structure are exemplified.

It is to be understood that all statements made herein concerning the capabilities of the addition agents presuppose the use of one or a mixture

of two or more from each class. The carrying agents produce a degree of brightness without any brightener but not enough to be satisfactory alone. I prefer the use of the more common and readily available compounds, and prefer to employ in each addition agent class only compounds devoid of the group which characterizes the other addition agent class.

The constituents of the bath according to the preferred practice of the invention are (1) water, (2) nickel sulfate, nickel chloride or nickel sulfate with nickel chloride, (3) an aromatic sulfonyl compound such as an aromatic sulfonic acid or a nickel, alkali metal, or cobalt salt thereof, an aromatic sulfonamide, or sulfimide, or a mixture of a plurality thereof, (4) a wetting agent, and (5) a polyalkylene amine or a mixture of polyalkylene amines. An additional ingredient of the solution which is desirable is a buffering agent such as boric acid, formic acid, ammonium sulfate, or the like.

It will be noted that in respect to major constituents, the solutions are similar to the well known "all sulfate," "all chloride," and "sulfate-chloride" or Watts type nickel plating solutions. It will be noted also that as to the aromatic sulfonyl type of addition agent or "carrier" as it is often called, the group of suitable materials are of the type which is represented by well known carriers in the bright nickel plating industry. The essential novel feature of the present invention is the use in such solutions of a small amount of a polyalkylene amine or a mixture of polyalkylene amines of molecular weight from about 100 to about 1800 or even higher.

The preferred basic solutions in connection with which my invention is realized are as follows:

All sulfate

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	100 to 400 gms., preferably 200 to 300 gms.
Boric acid.....	0 to 60 gms., preferably 10 to 40 gms.
Wetting agent (e. g. sodium lauryl sulfate).....	0 to 5 gms., preferably 0.5 to 1 gm.
H_2O to make 1000 cc.	

All chloride

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	50 to 250 gms., preferably 100 to 200 gms.
Boric acid.....	0 to 60 gms., preferably 10 to 40 gms.
Wetting agent (e. g. sodium lauryl sulfate).....	0 to 5 gms., preferably 0.5 to 1.0 gm.
H_2O to make 1000 cc.	

Sulfate-chloride (Watts type)

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	100 to 400 gms., preferably 200 to 300 gms.
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	10 to 90 gms., preferably 25 to 40 gms.
Boric acid.....	0 to 50 gms., preferably 15 to 40 gms.
Wetting agent (e. g. sodium lauryl sulfate).....	0.5 to 0 gm., preferably 0.05 to 0.15 gm.

To each of the foregoing basic solutions I add a suitable quantity of each, or a mixture of two or more of each, of the two cooperating addition agents. One of said addition agents or mixtures is one of the aromatic sulfonyl type and the other is of the alkylene amine type described above. The solution should, for best results, contain an anti-pit agent although the deposits may be suitable for some purposes without eliminating the pitting and, under some conditions, the deposits may not be objectionably pitted even in the absence of an addition agent for control of pitting. Sodium lauryl sulfate may be used as an anti-pit agent, although, as stated, its use is not essential and other wetting agents or mixtures of wetting agents may be used for control of pitting.

The following specific examples will serve to illustrate the invention.

TABLE II

Solution No.	1	2	3	4	5	6	7	8	9	10
Nickel Sulfate .6H ₂ O	240	240	240	240	240	240	240	240	240	240
Nickel Chloride .7H ₂ O	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5
Boric Acid	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5
Sodium Lauryl Sulfate	15									
Tetraethylene Pentamine Condensed with the following in the Molecular Ratio Indicated:										
Acrylonitrile (1:7)	.00075									
Methyl Sulfate (1:12)		.005								
Epichlorohydrin (1:2)			.01							
Epichlorohydrin and Phenol (1:1:1)				.003						
Benzene Sulfonyl Chloride (1:2)					.006					
Chloroacetic Acid and Methyl Sulfate (1:2:2)						.005				
Dimethyl Chloroacetal (1:2)							.01			
Tetraethylene Pentamine (Monomer)								.02		
Polymerized Tetraethylene Pentamine of Molecular Weight 1200									.005	
Polymerized Tetraethylene Pentamine of Molecular Weight 1800										.006
Sulfonated Naphthalene (NI) ¹	5.0	5.0	2.0	5.0	5.0	5.0	5.0	2.0	5.0	5.0
pH	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Temperature (Degrees Fahrenheit)	140	140	140	140	140	140	140	140	140	140
C. D.	40	40	40	40	40	40	40	40	40	40

¹ "Sulfonated naphthalene" is a composition such as may be produced by reacting 2 parts of 20% oleum on one part of naphthalene at 160° C. for two hours, neutralizing the resulting mixture with nickel carbonate, filtering and diluting to 26° B_é. Where quantities of "sulfonated naphthalene" are referred to herein, it is to be understood that the quantity specified represents roughly the nickel-naphthalene-mixed-sulfonate content of the mixture.

TABLE III

Solution No.	1	2	3	4	5	6	7	8
Nickel Sulfate .6H ₂ O	240	240	240	240	240	240	240	240
Nickel Chloride .7H ₂ O	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5
Boric Acid	37.5	37.5	37.5	37.5	37.5	37.5	37.5	37.5
Ammonium Sulfate	22.5							
Formic Acid			1					
Citric Acid				2				
Formalin							3	
Sodium Lauryl Sulfate	.1	.1	.1	.1	.1	.05	.05	.1
Tetraethylene Pentamine Condensed with Acrylonitrile in Molecular Ratio of 1:7	.0001	.001	.001	.001	.001	.0005	.001	.001
β-Naphthalene Monosulfonate (NI)		.75						
α-Chloronaphthalene Monosulfonate (NI)					1.0			
α-Chloronaphthalene Disulfonate (NI)						1.5		
Sulfonated Naphthalene ¹	5	5	5	5	5	5	5	5
Saccharin								1
pH	3.5	3.0	4.0	4.0	3.0	3.0	3.0	3.5
Temperature (Degrees Fahrenheit)	140	140	140	140	140	140	140	140
C. D.	40	40	40	40	40	40	40	40

¹ "Sulfonated naphthalene" is a composition such as may be produced by reacting 2 parts of 20% oleum on one part of naphthalene at 160° C. for two hours, neutralizing the resulting mixture with nickel carbonate, filtering and diluting to 26° B_é. Where quantities of "sulfonated naphthalene" are referred to herein, it is to be understood that the quantity specified represents roughly the nickel-naphthalene-mixed-sulfonate content of the mixture.

From the foregoing it will be obvious that I have provided an improved process for electro-deposition of bright nickel, and, while I have described my invention with reference to present preferred embodiments, I wish it understood that these are only illustrative; and I desire to be limited only in accordance with the spirit and scope of the appended claims.

Having thus described my invention, what I claim is:

1. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a polyalkylene amine of the class consisting of unsubstituted amines of the general form

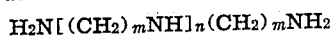


where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, and polyalkylene amines which are the condensation products

produced by reacting a polyalkylene amine of said general form with a material of the class consisting of epichlorohydrin, acrylonitrile, methyl sulfate, chloroacetic acid, epichlorohydrin with phenol, dimethyl chloroacetal, benzene sulfonyl chloride, and styrene oxide, soluble in said solution to the extent of at least 0.0001 gram per liter, and having a molecular weight from 100 to 1800, and the other of said addition agents being an organic compound of the class consisting of benzene mono-sulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para-chloro-benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naphthalene-1,5-disulphonic acid, sulfonated naphthalene, alpha-naphthalene mono-sulfonic acid, beta-naphthalene monosulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel, and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0001 to 0.1 gram per liter, and said second

mentioned addition agent being present in concentration from 0.2 to 15 grams per liter.

2. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a polyalkylene amine of the class consisting of unsubstituted amines of the general form



where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, and polyalkylene amines which are the condensation products produced by reacting a polyalkylene amine of said general form with a material of the class consisting of epichlorhydrin, acrylonitrile, methyl sulfate, chloroacetic acid, epichlorhydrin with phenol, dimethyl chloroacetal, benzene sulfonyl chloride, and styrene oxide soluble in said solution to the extent of at least 0.0005 gram per liter, and having a molecular weight from 600 to 1800, and the other of said addition agents being an organic compound of the class consisting of benzene mon-sulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naphthalene-1,5-disulphonic acid, sulfonated naphthalene, alpha naphthalene monosulfonic acid, beta naphthalene mono sulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel, and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0005 to 0.05 gram per liter, and said second mentioned agent being present in concentration from 0.2 to 15 grams per liter.

3. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being an unsubstituted polyalkylene amine composition of the general form



where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, of molecular weight from 100 to 1800, and the other of said addition agents being an organic compound of the class consisting of benzene monosulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, di-

phenyl sulfone, naphthalene - 1,5 - disulphonic acid, sulfonated naphthalene, alpha naphthalene monosulfonic acid, beta naphthalene mono sulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel, and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0001 to 0.1 gram per liter, and said second mentioned addition agent being present in concentration from 0.2 to 15 grams per liter.

4. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being an unsubstituted polyalkylene amine composition of the general form



where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, of molecular weight from 600 to 1800, and the other of said addition agents being an organic compound of the class consisting of benzene mono-sulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naphthalene - 1,5 - disulphonic acid, sulfonated naphthalene, alpha naphthalene monosulfonic acid, beta naphthalene mono sulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel, and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0005 to 0.05 gram per liter, and said second mentioned agent being present in concentration from 0.2 to 15 grams per liter.

5. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a condensation product of a polyalkylene amine of the general form

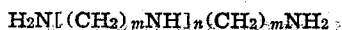


where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, with acrylonitrile, and the other of said addition agents being an organic compound of the class consisting of benzene mono-sulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naph-

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thalene-1,5-disulphonic acid, sulfonated naphthalene, alpha naphthalene monosulfonic acid, beta naphthalene mono-sulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel, and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0001 to 0.1 gram per liter, and said second mentioned addition agent being present in concentration from 0.2 to 15 grams per liter.

6. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a condensation product of a polyalkylene amine of the general form



where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, with acrylonitrile, and the other of said addition agents being an organic compound of the class consisting of benzene monosulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naphthalene-1,5-disulfonic acid, sulfonated naphthalene, alpha naphthalene monosulfonic acid, beta naphthalene mono-sulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0005 to 0.05 gram per liter, and said second mentioned agent being present in concentration from 0.2 to 15 grams per liter.

7. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a condensation product of a polyalkylene amine of the general form



where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, with epichlorhydrin, and the other of said addition agents being an organic compound of the class consisting of benzene monosulfonic acid, benzene disulfonic acids, monochlor benzene mono-sulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naphthalene-1,5-disulfonic acid, sulfonated

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naphthalene, alpha naphthalene monosulfonic acid, beta naphthalene mono sulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0001 to 0.1 gram per liter, and said second mentioned addition agent being present in concentration from 0.2 to 15 grams per liter.

8. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a condensation product of a polyalkylene amine of the general form



where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, with epichlorhydrin, and the other of said addition agents being an organic compound of the class consisting of benzene monosulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naphthalene-1,5-disulfonic acid, sulfonated naphthalene, alpha naphthalene monosulfonic acid, beta naphthalene mono-sulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0005 to 0.05 gram per liter, and said second mentioned agent being present in concentration from 0.2 to 15 grams per liter.

9. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a condensation product of a polyalkylene amine of the general form



where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, with methyl sulfate, and the other of said addition agents being an organic compound of the class consisting of benzene monosulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naphthalene-1,5-disulfonic acid, sulfonated naphthalene, alpha naphthalene monosulfonic acid,

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beta naphthalene monosulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0001 to 0.1 gram per liter, and said second mentioned addition agent being present in concentration from 0.2 to 15 grams per liter.

10. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a condensation product of a polyalkylene amine of the general form



where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, with methyl sulfate, and the other of said addition agents being an organic compound of the class consisting of benzene monosulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naphthalene-1,5-disulfonic acid, sulfonated naphthalene, alpha naphthalene monosulfonic acid, beta naphthalene monosulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0005 to 0.05 gram per liter, and said second mentioned agent being present in concentration from 0.2 to 15 grams per liter.

11. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a condensation product of a polyalkylene amine of the general form



where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, with styrene oxide, and the other of said addition agents being an organic compound of the class consisting of benzene monosulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene

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disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naphthalene-1,5-disulfonic acid, sulfonated naphthalene, alpha naphthalene monosulfonic acid, beta naphthalene monosulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel, and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.001 to 0.1 gram per liter, and said second mentioned addition agent being present in concentration from 0.2 to 15 grams per liter.

12. A method for electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment and which comprises electrolyzing an aqueous, acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixtures of nickel sulfate with nickel chloride, said solution also containing cooperating addition agents capable of imparting brightness to the deposit, one of said addition agents being a condensation product of a polyalkylene amine of the general form



where m is an integer from 2 to 4 inclusive and n is an integer greater than 2, with styrene oxide, and the other of said addition agents being an organic compound of the class consisting of benzene monosulfonic acid, benzene disulfonic acids, monochlor benzene monosulfonic acids, benzene monosulfonamide, saccharine, dichloro benzene disulfonic acids, 2,5-dibromo benzene sulfonic acid, toluene sulfonic acids, benzaldehyde sulfonic acids, diphenyl sulfonic acids, benzene sulfonyl chloride, para chloro benzene sulfonamide, xylene sulfonamides, para toluene sulfonamide, thiophene sulfonic acids, diphenyl sulfone, naphthalene-1,5-disulfonic acid, sulfonated naphthalene, alpha naphthalene monosulfonic acid, beta naphthalene monosulfonic acid, o-toluene sulfonamide, chloro naphthalene disulfonates and the sodium, potassium, nickel and cobalt salts thereof, said first mentioned addition agent being present in concentration from 0.0005 to 0.05 gram per liter, and said second mentioned agent being present in concentration from 0.2 to 15 grams per liter.

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