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ELECTRODEPOSITION OF NICKEL

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This invention relates to electrodeposition of nickel and more especially to the provision of a novel process and solution for electrodeposition of nickel principally characterized in that a novel combination of addition agents is employed for production of bright and ductile deposits, the same being fully bright as taken from the electroplating solution without buffing or other treatment for bringing up the brightness.

I have now discovered that by the use of polyethylene glycols of high molecular weight in combination with an auxiliary brightener of the aromatic sulfonate type, very excellent, smooth, bright and ductile deposits of nickel are obtained.

So far as I am aware, it has never been realized prior to my invention that polyethylene glycols of high molecular weight are useful as brightening addition agents in nickel plating. These compounds, being known as wetting agents were tested as anti-pit agents in acid nickel plating and found to be effective to prevent pitting only at such high concentrations as to produce excessive brittleness. I have discovered, however, that when these compounds are used in lower concentrations suitable for producing bright and ductile nickel deposits in cooperation with compounds of the aromatic sulfonate type, and anti-pit agents of the alcohol sulfate type are employed, the deposits are superior in both brightness and freedom from pitting.

The class of addition agents above referred to as aromatic sulfonate type compounds may be defined as compounds of the form $ArSO_2$—, where Ar represents an aromatic radical having not less than 6 nor more than 10 carbon atoms in the aromatic nucleus, such compound being soluble in the plating solution to the extent of at least 0.2 gram per liter. The free valence may be satisfied by various groups, for example OH, and NH—, or OM where M can be for example sodium, potassium, nickel, iron, or cobalt. The NH— group may be NH_2 or $NHSO_2Ar$, Ar having the same significance as before. The aromatic radicals represented by Ar in the above formula may be benzene or naphthalene radicals unsubstituted, or part of the hydrogen may be replaced by substituents such as chlorine, bromine, methyl, and ethyl radicals, etc.

Specific examples are set forth in Table I.

TABLE I

1. Naphthalene 1,5-disulfonic acid
2. Naphthalene 2,7-disulfonic acid
3. Diphenyl sulfone disulfonic acids
4. Benzaldehyde monosulfonic acids
5. Benzene monosulfonic acids
6. Toluene monosulfonamide
7. Ortho benzosulfimide, sodium salt
8. Nickel naphthalene disulfonic acids
9. Dibenzene sulfonamide ($PhSo_2NHSO_2Ph$)
10. $C_6H_5SO_2NHSO_2C_6H_4SO_2NHSO_2C_6H_5$ (bi dibenzene sulfonamide)

11. $C_6H_5SO_2NHSO_2C_6H_4C_6H_4SO_2NHSO_2C_6H_5$ (double dibenzene sulfonamide)
12. $C_6H_5SO_2NHSO_2C_6H_4OC_6H_4SO_2NHSO_2C_6H_5$ (dibenzene sulfonamide ether)

The class of compounds referred to above as the high molecular weight polyethylene glycols may be defined as polymeric compounds predominantly composed of the group CH_2CH_2O, preferably compounds of the form $R(CH_2CH_2O)_nH$, where n is an integer from 10 to 100 and R is a radical selected from the class consisting of radicals of the form R'O and R'NH, where R' is selected from the class consisting of hydrogen, alkyl radicals having from 1 to 20 carbon atoms, and aryl radicals having from 1 to 20 carbon atoms. In these compounds, replaceable hydrogen may be replaced by alkyl groups having from 1–5 carbon atoms, to the extent of 20% or less of the number of replaceable hydrogens. Such compounds must be soluble in the bath to the extent of at least .001 gram per liter and preferably are of molecular weight from 1000 to 6000. From 1% to 50% of the CH_2CH_2O groups may be replaced by $CH_2CH_2CH_2O$ groups.

Examples are set forth in Table II:

TABLE II

Polyethylene glycol, molecular weight 1000
Polyethylene glycol, molecular weight 500
$PhO(CH_2CH_2O)_nH$, n being an integer from 10 to 100
$PhNH(CH_2CH_2O)_nH$, n being an integer from 10 to 100

Compounds like the foregoing examples where from 1 to 50% of the CH_2CH_2O groups are replaced by

$CH_2CH_2CH_2O$

groups.

The addition agents referred to above as alcohol sulfates may be defined as the normal, primary, aliphatic, alcohol sulfates having from 8 to 18 carbon atoms in the molecules, for example:

1. Sodium lauryl sulfate.
2. A mixture of normal, primary, aliphatic, alcohol sulfates derived from cocoanut oil and containing approximately 45% sodium lauryl sulfate, the balance substantially the sodium alcohol sulfates of higher and lower aliphatic alcohols having from 8 to 18 carbon atoms.

The above described addition agents may be used in nickel plating solutions of the nickel sulfate, nickel chloride, and mixed nickel sulfate-nickel chloride types. The basic solutions, according to the present invention, are as follows:

All sulfate

$NiSO_4.7H_2O$: 100 to 400 gms., preferably 200 to 300 gms.
Boric acid: 0 to 6 gms., preferably 10 to 40 gms.
Wetting agent of the lauryl sulfate type: 0 to 0.5 gm., preferably 0.05 to 0.2 gm.
Brightener of the aromatic sulfonate type: 0.2 gm. to saturation, preferably 0.5 to 15 gms.
Brightening agent of the polyethylene glycol type: .001 to .05 gm., preferably 0.002 to 0.03 gm.
H_2O to make 1000 cc

All chloride

$NiCl_2.6H_2O$: 50 to 250 gms., preferably 100 to 200 gms.
Boric acid: 0 to 60 gms., preferably 10 to 40 gms.
Wetting agent of the lauryl sulfate type: 0 to 0.5 gm., preferably 0.05 to 0.2 gm.
Brightener of the aromatic sulfonate type: 0.2 gm. to saturation, preferably 0.5 to 15 gms.
Brightener of the polyethylene glycol type: .001 to .05 gm., preferably 0.002 to 0.03 gm.
H_2O to make 1000 cc.

Sulfate-chloride (Watts type)

$NiSO_4.7H_2O$: 100 to 400 gms., preferably 200 to 300 gms.

$NiCl_2.6H_2O$: 10 to 60 gms., preferably 25 to 40 gms.

Boric acid: 0 to 50 gms., preferably 15 to 40 gms.

Wetting agent of the lauryl sulfate type: 0 to 0.5 gm., preferably 0.05 to 0.2 gm.

Brightener of the aromatic sulfonate type: 0.2 gm. to saturation, preferably 0.5 to 15 gms.

Brightener of the polyethylene glycol type: .001 to .05 gm., preferably 0.002 to 0.003 gm.

H_2O to make 1000 cc.

The following table indicates specific compositions suitable for use in the practice of the invention:

	1	2	3	4	5	6	7	8
Nickel sulfate heptahydrate	250	250	250	250	250	250	250	250
Nickel chloride hexahydrate	40	40	40	40	40	40	40	40
Boric acid	40	40	40	40	40	40	40	40
Sodium lauryl sulfate	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Naphthalene 1,5-disulfonic acid	1.0				0.5			
Saccharine, sodium salt		0.5				1.0		
Dibenzene sulfonamide			1.0				1.5	
Bi-dibenzene sulfonamide				1.0				1.0
$HO(CH_2CH_2O)_{20}H$	.01	.02						
$PhO(CH_2CH_2O)_{20}H$			.01	.01				
$HO(CH_2CH_2O)_{30}H$					.01		.02	
$PhNH(CH_2CH_2O)_{20}H$						.01		.02

Having thus described the invention, what is claimed is:

1. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment, which method 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 compound of the form $ArSO_2$—, where Ar represents an aromatic radical containing not less than 6 nor more than 10 carbon atoms in the aromatic nucleus, such compound being dissolved in said solution to the extent of at least 0.2 gram per liter and the other of said agents being a compound of the form $R(CH_2CH_2O)_nH$, where n is an integer from 10 to 100 and R is a radical selected from the class consisting of radicals of the form R'O and R'NH where R' is selected from the class consisting of hydrogen, alkyl radicals having from 1 to 20 carbon atoms, and aryl radicals having from 1 to 20 carbon atoms, said last mentioned addition agent being dissolved in said solution to the extent of from 0.001 to 0.05 gram per liter.

2. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment, which method comprises electrolyzing an aqueous acid solution of a nickel electrolyte of the class consisting of nickel sulfate, nickel chloride, and mixture 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 compound of the form $ArSO_2$—, where Ar represents an aromatic radical containing not less than 6 nor more than 10 carbon atoms in the aromatic nucleus, such compound being dissolved in said solution to the extent of from 0.2 to 15 grams per liter and the other of said addition agents being a compound of the form $RO(CH_2CH_2O)_nH$, where n is an integer from 10 to 100 and R is hydrogen, said last mentioned addition agent being dissolved in said solution to the extent of from 0.001 to 0.05 gram per liter.

3. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment, which method 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 compound of the form $ArSO_2$—, where Ar represents an aromatic radical containing not less than 6 nor more than 10 carbon atoms in the aromatic nucleus, such compound being dissolved in said solution to the extent of from 0.2 to 15 grams per liter and the other of said addition agents being a compound of the form $RO(CH_2CH_2O)_nH$, where n is an interger from 10 to 100 and R is an alkyl radical having from 1 to 20 carbon atoms, said last mentioned addition agent being dissolved in said solution to the extent of from 0.001 to 0.05 gram per liter.

4. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment, which method 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 compound of the form $ArSO_2$—, where Ar represents an aromatic radical containing not less than 6 nor more than 10 carbon atoms in the aromatic nucleus, such compound being dissolved in said solution to the extent of from 0.2 to 15 grams per liter and the other of said addition agents being a compound of the form $RO(CH_2CH_2O)_nH$, where n is an aryl radical having from 1 to 20 carbon atoms, said last mentioned agent being dissolved in said solution to the extent of from 0.001 to 0.05 gram per liter.

5. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment, which method 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 compound of the form $ArSO_2$—, where Ar represents an aromatic radical containing not less than 6 nor more than 10 carbon atoms in the aromatic nucleus, such compound being dissolved in said solution to the extent of from 0.2 to 15 grams per liter and the other of said addition agents being a compound of the form $R(CH_2CH_2O)_nH$, where n is an integer from 10 to 100 and R is R'NH, R' being an alkyl radical having from 1 to 20 carbon atoms, said last mentioned addition agent being dissolved in said solution to the extent of from 0.001 to 0.05 gram per liter.

6. A method of electrodepositing nickel in the form of a deposit which is bright as taken from the plating solution without further treatment, which method 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 compound of the form $ArSO_2$—, where Ar represents an aromatic radical containing not less than 6 nor more than 10

carbon atoms in the aromatic nucleus, such compound being dissolved in said solution to the extent of from 0.2 to 15 grams per liter and the other of said addition agents being a compound of the form $R(CH_2CH_2O)_nH$, where n is an integer from 10 to 100 and R is R'NH, R' being an aryl radical having from 1 to 20 carbon atoms, said last mentioned addition agent being dissolved in said solution to the extent of from 0.001 to 0.05 gram per liter.

References Cited in the file of this patent

UNITED STATES PATENTS

2,524,619	Brown	Oct. 3, 1950
2,686,757	Cook et al.	Aug. 17, 1954