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ALKALINE NICKEL PLATING SOLUTIONS

Arthur H. DuRose, Richmond Heights, and Robert L. Stern, Cleveland Heights, Ohio, assignors to Kewanee Oil Company, Bryn Mawr, Pa.

No Drawing. Continuation of abandoned application Ser. No. 752,168, Aug. 13, 1968. This application July 22, 1971, Ser. No. 165,383

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U.S. Cl. 204—49 6 Claims

ABSTRACT OF THE DISCLOSURE

Addition agents for use in alkaline nickel plating baths which produce a brighter more ductile nickel electroplate. The addition agents are of the general formula:

$$R-C\equiv C-R_1$$

$$R_4-\underset{\displaystyle R_7}{\overset{}{C}}=\underset{\displaystyle R_8}{\overset{}{C}}-CH_2-OH$$

and

$$R_9-CH=CH-C\equiv C-R_{10}$$

Typical compounds include 2-chloroallyl alcohol; 1-ethynyl-1-cyclohexanol; 2-butyne-1,4-diol; 2,4-hexadiyne-1,6-diol and 2-methoxy-1-butene-3-yne.

This is a continuation of application Ser. No. 752,168 filed Aug. 13, 1968, now abandoned.

This invention relates to the electrodeposition of nickel and nickel-cobalt alloys from alkaline plating solutions containing a variety of addition agents which includes certain acetylenic or olefinic alcohols and ethers. More specifically, this invention is concerned with improving the brightness of nickel deposits produced from alkaline baths and increasing the limiting current density of said baths.

Alkaline nickel plating solutions have inherent advantages. The throwing power of such solutions is almost invariably better than that observed in acid nickel solutions of the Watts or all-chloride variety. For example, the throwing power for alkaline nickel solutions using the BSI formula ranges from 15 to 70% while that for the Watts solution is −5 to +5%. Moreover, when proper pre-plating steps are followed, a number of alkaline nickel formulations can be used to plate nickel directly on zinc base die castings. This provides a distinct economic advantage as it avoids the need for the use of cyanide copper which not only eliminates the costly problem of waste disposal but affords a better corrosion resistance.

Many complex alkaline nickel plating solutions of various formulations have been proposed and devised heretofore. Their use, however, has not been extensive for several reasons, primarily because of a limited current density, lack of ductility, high stress and lack of lustre in the deposit.

A variety of complexing agents has been used, see Saubestre's review in Plating, May 1958. Complexing agents which have been used singly or in combination with others are: NH_4OH (Brit. 512,484), triethanolamine as described in J. Met. Fin. Soc. Japan 11 (2) 55 (1960), citrate (Brit. 880,786), hydroxyethylethylenediaminetriacetic acid (Brit. 1,022,073), and polyamines (U.S. 2,335,070). Also ammonia, citrate and pyrophosphate are used in combination as described in U.S. 2,069,566 and Brit. 902,499. Similarly citrate, alkanolamines and EDTA type compounds are described in U.S. 2,773,818.

Other complexing agents such as glycolic acid, tartarate, acetylacetone, and ethylenediamine may be used. Even glycerol and oxalate can be used although they are used in combination with other agents having more complexing ability and solubility.

Little work has been done on producing bright or semibright nickel deposits from alkaline solutions. Brit. 902,499 proposes the use of saccharin in combination with selenium, tellurium, arsenic or coumarin, while Brit. 880,786 uses saccharin and a rather high concentration of formaldehyde.

At first thought one might assume that any addition agent or brightener that is useful in acid nickel plating solutions would be also useful and effective in alkaline nickel solutions. This assumption has been shown many times not to be true. In fact many brighteners and addition agents which are effective in acid baths of zinc, tin, antimony, copper and lead are ineffective and useless in the corresponding alkaline baths. Nickel is no exception. Table I is a list of compounds which exhibit little or not effect in alkaline nickel solutions.

TABLE I

(1) Phenylpropiolic acid (propiolic good)
(2) 3-methoxy-3-phenyl butyne-1
(3) N-propargyldibenzenesulfonamide
(4) 2-(2-propynyl)thiobenzothiazole
(5) Allylsulfonate
(6) Diallyl allyl phosphonate
(7) Allylarsonic acid
(8) β-Neopentylallyl alcohol
(9) 4-methyl-4-pentene-2-ol
(10) Undecyl-10-ene-1-ol
(11) Methylbuteneol
(12) Triallylamine
(13) Tetraallylethylenediamine
(14) N allyl saccharin
(15) Cinnamyl alcohol
(16) Crotonic acid
(17) Butanediol
(18) Glycerine
(19) Cyclohexanol
(20) Fuchsin
(21) Phenol
(22) Nitroindazole
(23) Tetramethylene-bis-pyridinium chloride
(24) Benzene sulfinic acid
(25) Thiourea
(26) Polyglycols and pluronics

It should be noted that compounds 1–7, 12–14, 20–26 of above table are useful in acid nickel baths.

An important difference between the alkaline and acid nickel solutions is that there appears to be very little, or consistent synergistic effect due to the combination of so-called acid nickel control agents and brighteners when they are used in combination in the alkaline nickel solution. In acid nickel solutions the use of the brightener alone (such as fuchsin, ethoxylated propargyl alcohol,

ethylenecyanohydrin, etc.) usually gives only a slight increase in or uneven deposit brightness and the deposit tends to be brittle. When a control agent such as naphthalene sulfonate or saccharin is added the brightness and uniformity of brightness are enhanced and the ductility is improved. Very seldom is the above combination of any benefit in the alkaline nickel solution. For example ethoxylated butynediol at .2 g./l. gives a bright deposit up to about 70 a.s.f. At higher current densities the deposit becomes duller. By acid nickel standards the ductility is poor. When 1 g./l. of saccharin is added the deposit becomes duller especially in the low current density area and slightly less ductile. A similar effect, i.e., no improvement, is noted when 3 g./l. of N,N'-bis-(phenylsulfonyl-4,4'-biphenyldisulfonimide is added to an alkaline nickel solution containing butynediol. Tetramethylene-bis-pyridinium chloride effects a streaked, semi-bright, very brittle deposit. The addition of N,N'-bis-(phenylsulfonyl)-4,4'-biphenyldisulfonimide seemed to relieve the brittleness somewhat but darkened the deposit. N-propargyl saccharin effects a bright deposit at .1 g./l. with air agitation and the addition of N,N'-bis(phenylsulfonyl)-4,4'-biphenyldisulfonimide causes no improvement in ductility or brightness. For some reason N-allyl saccharin which is similar to N-propargyl saccharin when used in the acid bath, has no effect when used in the alkaline solution.

In many cases as indicated above the addition of the sulfonate or sulfonamide control agent was harmful or of no help. In one case using 3 cc./l. of allyl alcohol the deposit was semibright but the addition of a sulfonamide increased the brightness. This was not so for B-chloroallyl alcohol where only 0.5 cc./l. of the alcohol had to be used. The use of N,N'-bis-(phenylsulfonyl)-4,4'-biphenyldisulfonimide will eliminate misplating caused by high concentrations of ethoxylated propargyl alcohol but just as good deposits are obtained when lower concentrations of the acetylenic compound are used with no sulfonimide. Another case where a control agent was beneficial was for 2-butyne-1,4-dithioethanol. These cases are rare however.

The use of certain sulfonate and sulfonamide control agents alone, in alkaline nickel solutions has little effect compared to when these are used in acid solutions. The deposit from alkaline solutions with no addition agents present usually has more sheen than those from acid solutions. This may be why the addition of such agents as benzene sulfonate, saccharin or allyl sulfonate very seldom exhibit any improvement in brightness. Sometimes, as for dibenzenesulfonamide the uniformity of lustre is improved but the increase in lustre is almost negligible. Also the ductility is not improved.

In some cases there is an advantage in using two brighteners in the alkaline nickel solution. For example many of the acetylenic or olefinic compounds such as diethylamino-3-butyne-4-ol or butenediol effect bright deposits except at the high current density of about 70–80 a.s.f. Ethylenecyanohydrin on the other hand gives brighter deposits at the higher current density than at lower current density. Therefore there is an advantage in using say butenediol and ethylenecyanohydrin in combination.

The addition agents of the present invention comprise unsaturated organic compounds selected from the group consisting of:

(A) $R-C\equiv C-R^1$

wherein

R is selected from the group consisting of hydrogen, lower alkyl of one to three carbon atoms

$-C\equiv C-R^1$, $-CH_2N\begin{matrix}R^4\\R^5\end{matrix}$, and R^1

R^1 is a radical of the formula

$$-\overset{R^2}{\underset{R^3}{C}}-(XC_nH_{2n})_yZ$$

R^2 and R^3 are independently selected from the group consisting of hydrogen and lower alkyl of one to three carbon atoms,

X is selected from the group consisting of oxygen and sulfur,

n is an integer from 0 to 2,

y is an integer from 0 to 4, provided that when *n* is 1, *y* is 1,

Z is selected from the group consisting of hydroxyl and

$$-\overset{\overset{O}{\|}}{C}NH_2,$$

R^4 is selected from the group consisting of hydrogen and lower alkyl containing one to three carbon atoms, and R^5 is a lower alkyl containing one to three carbon atoms,

(B)
$$R^6-\overset{R^7}{C}=\overset{R^8}{C}-CH_2-OH$$

wherein

R^6 is selected from the group consisting of hydrogen and $-CH_2OH$, and

R^7 and R^8 are independently selected from the group consisting of hydrogen and halogen, and

(C) $R^9-CH=CH-C\equiv C-R^{10}$

wherein

R^9 is alkoxy containing one or two carbon atoms,

R^{10} is selected from the group consisting of hydrogen and

$$-CH_2N\begin{matrix}R^{11}\\R^{12}\end{matrix}$$

R^{11} is selected from the group consisting of hydrogen and alkyl containing from one to three carbon atoms, and

R^{12} is an alkyl containing from one to three carbon atoms.

These addition agents of the instant invention are utilized to advantage in alkaline nickel plating processes. Such a nickel plating process can utilize any conventional source of nickel as used in the plating industry such as $NiCl_2$, $NiSO_4$ or $NiBF_4$ wherein the pH is adjusted to between about 7.0 and 11.0. Such plating baths can be operated generally in the range from room temperature to 180° F. depending on the particular type bath employed. Likewise, plating can be accomplished in such baths at current densities of from about 5 to about 100 amps per sq. ft.

This invention will be more fully described by the following examples. They are given by way of illustration, but not of limitation. Unless otherwise specified all temperatures are in Fahrenheit and all parts and percentages are by weight.

EXAMPLE 1

A solution of the following composition and conditions was used:

$NiSO_4 \cdot 6H_2O$ ---------- g./l.	100
EDTA (Na_4) (sodium salt of ethylene diamine tetra-acetic acid) ---------- g./l.	40
Sodium citrate ---------- g./l.	60
Ammonium chloride ---------- g./l.	35
Triethanolamine ---------- g./l.	35
pH ----------	8.0
Temperature ---------- ° F.	140

When a bent panel was plated in this solution using air agitation and at such a current that the current density range was from 5 to 100 a.s.f., a dull semibright deposit was obtained at 20–80 a.s.f., a brighter deposit at 5–20 a.s.f. and a dull matte deposit at 80–100 a.s.f. The throwing power (BSI) of the solution is 45%. When a lower temperature or less agitation is used the above C.D. ranges are lowered and the deposit may be "burnt" on the high C.D. edges.

EXAMPLE 2

1-methoxy-5-diethylaminopentene-3-yne was added to the solution of Example 1. A concentration of 0.03 g./l. effected a bright deposit except at the high C.D. areas where the deposit was semibright. 0.2 g./l. was necessary to produce brightness at the high C.D. of about 70–90 a.s.f. At this concentration the deposit was still brittle and the addition of control agents such as naphthalene disulfonate and saccharin did no good.

EXAMPLE 3

To the solution of Example 1, .1 g./l. of 2-butenediol-1,4-was added and a deposit produced which was bright except for the high C.D. edges. When 3% N,N'-bis(phenylsulfonyl)-4,4'-biphenyldisulfonimide was added the deposit became duller but then if the butenediol was increased to 0.25 g./l. a fully bright deposit, except for the extreme low C.D., could be produced.

EXAMPLE 4

A similar but slightly less uniform deposit to that obtained in Example 3 under the same conditions was produced by using 0.01 g./l. of butynediol in place of butenediol but the use of a control agent was not advantageous.

EXAMPLE 5

A nickel solution was formulated by use of the following:

	G./l.
Citric acid	89.3
Commercial nickel carbonate	49.6
$NiSO_4 \cdot 6H_2O$	60

K_2CO_3 to give a pH of 7.5.
Temp. 140° F.—Air agitation.

When a bent panel was plated in this solution at an average C.D. of 40 a.s.f., a fairly uniform dull deposit was obtained. The addition of 0.1 g./l. of butynediol caused the deposit to be sembibright and .5 g./l. effected a uniform bright deposit.

EXAMPLE 6

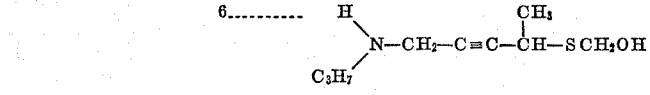
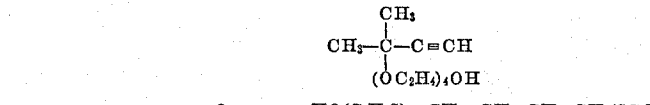
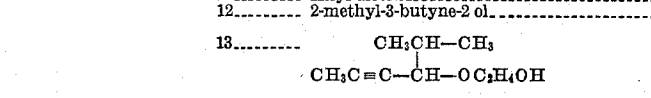
A nickel solution according to U.S. 2,069,566 of the following composition was used:

$NiSO_4 \cdot 6H_2O$	g./l.	120
$Na_4P_2O_7 \cdot 10H_2O$	g./l.	65
Sodium citrate ($2H_2O$)	g./l.	60
Citric acid	g./l.	15
NaCl	g./l.	30
NH_4OH soln. (sp. g. 88)	cc./l.	70
pH		8.0

Temp. 50° C.; slow air agitation.

A bent panel was plated at 20 a.s.f. average. The deposit was bright from 1 to 12 a.s.f. and grey above this C.D. When 0.005 g./l. of propargyl alcohol was added the deposit was fully bright. When 0.3 g./l. of coumarin was further added the deposit lost some lustre in the high C.D. area, i.e., 30–50 a.s.f., where it might be described as bright-semibright.

Additional compounds falling within the scope of the instant invention and their effective concentration ranges as well as optimum concentrations are given hereinafter.

		Grams/liter	
		Range	Optimum
1	2,7-dimethylocta-3,5-diyne-2,7-diol	.005–.2	.1
2	Propargyl alcohol	.001–.02	.005
3	2,5-dimethyl hexyn-3-ol-2	.01–.2	.05
4	1,4-bis-(β-oxypropionamide)butyne-2	.05–.2	.1
5	Ethoxylated propargyl alcohol ($2C_2H_4O$—) $CH \equiv C-CH_2(OH_2H_4)_2OH$	.001–.08	.04
6		.03–2.0	0.8
7	Tetraethoxymethylbutynol 	.1–.5	.2
8	$HO(C_2H_4S)_2-CH_2-CH=CH-CH_2(SC_2H_4)_3-OH$	.02–.5	.15
9	Ethoxylated butynediol ($4C_2H_4O$—) $HO(C_2H_4O)_4-CH_2-C \equiv C-CH_2-(OC_2H_4)_4OH$	.05–.3	.5
10	2-chloroallyl alcohol	.1–.5	.3
11	Allyl alcohol	1–10	3.0
12	2-methyl-3-butyne-2 ol	.01–.2	.05
13		.05–0.5	0.1
14	1-ethynyl-1-cyclohexanol	.01–.05	.02
15	2-butene-1,4-diol	.02–.5	.15
16	3-butyne-2-ol	.01–.2	.03
17	2-butyne-1,4-diol	.01–.2	.05
18	2,4-hexadiyne-1,6-diol	.005–.2	.1
19	2-butyne-1,4-dithiodiethanol	.1–2.0	1.0
20	$CH_3O-CH=CH-C \equiv C-CH_2NH(C_3H_7)$	.03–0.5	0.15
21	4-diethylamino-1-hydroxybutyne-2	.03–.5	.15
22	2,3-dibromobutene-2-diol-1,4	0.01–0.5	0.15
23	1-methoxy-5-diethylaminopentene-3-yne	.01–.5	.2
24	1-methoxy-1-butene-3-yne	.05–.3	.1

To further show the non-equivalence of acid and alkaline nickel plating baths, a number of compounds of the instant invention, namely 2-butene-1,4-diol; 2,7-dimethyl-octa-3,5-diyne-2,7-diol; 2,4-hexadiyne-1,6-diol; 2-butyne-1,4-dithiodiethanol; propiolic acid; allyl alcohol; dimethyl hexynol and acetylene dicarboxylic acid were tested as additives in acid nickel baths and were found to be uneffective brighteners in acid nickel baths.

As stated earlier in the specification, any conventional source of nickel may be used in supplying the nickel for the plating bath for the instant invention. For example, nickel chlorate, nickel sulfate, nickel tetraborate, nickel carbonate, nickel hydroxide, nickel sulfamate and the like. Commonly, complexing agents are used in such plating baths to produce complex ions and such is suitable in the practice of the instant invention.

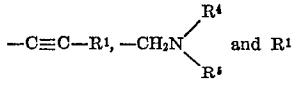
We claim:

1. An alkaline nickel electroplating bath including, in solution, an unsaturated organic brightener selected from the group consisting of:

(A) $R—C\equiv C—R^1$

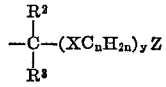
wherein

R is selected from the group consisting of hydrogen, lower alkyl or one to three carbon atoms,



and R^1

R^1 is a radical of the formula



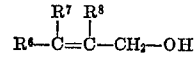
R^2 and R^3 are independently selected from the group consisting of hydrogen and lower alkyl of one to three carbon atoms, X is selected from the group consisting of oxygen and sulfur, n is an integer from 0 to 2, y is an integer from 0 to 4, provided that when n is 1, y is 1, and when y is 1 or more, n is at least 1,

Z is selected from the group consisting of hydroxyl and



R^4 is selected from the group consisting of hydrogen and lower alkyl containing one to three carbon atoms, and R^5 is a lower alkyl containing one to three carbon atoms,

(B)



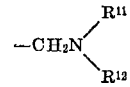
wherein

R^6 is selected from the group consisting of hydrogen and $—CH_2OH$, and

R^7 and R^8 are independently selected from the group consisting of hydrogen and halogen, and

(C) $R^9—CH=CH—C\equiv C—R^{10}$

wherein R^9 is alkoxy containing one or two carbon atoms, R^{10} is selected from the group consisting of hydrogen and



R^{11} is selected from the group consisting of hydrogen and alkyl containing one to three carbon atoms, and R^{12} is an alkyl containing from one to three carbon atoms, said organic brightener being present in said bath in an amount sufficient to provide a brighter, more ductile nickel electroplate.

2. The bath of claim **1** having a pH in the range of about 7.0 to 11.0.

3. A method of electrodepositing a brighter more ductile nickel electroplate which comprises electrolyzing the bath of claim **2** at a temperature of room temperature to 180° F.

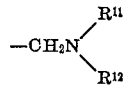
4. A bath for the electrodeposition of a nickel plate comprising an aqueous alkaline solution having a pH of between 7.0 and 11.0 including at least one electrolyte containing nickel ions and having dissolved therein a sufficient amount of a brightening agent comprising a unsaturated organic compound having the formula:

$R^9—CH=CH—C\equiv C—R^{10}$

wherein

R^9 is alkoxy containing from one to two carbon atoms,

R^{10} is selected from the group consisting of hydrogen and



R^{11} is selected from the group consisting of hydrogen and alkyl containing from one to three carbon atoms, and R^{12} is an alkyl containing from one to three carbon atoms.

5. The bath according to claim **4** wherein the addition agent is used in an amount of between 0.01 and 0.5 g./l. of solution.

6. The bath according to claim **4** wherein the addition agent consists of 1-methoxy-5-diethylaminopentene-3-yne.

References Cited

UNITED STATES PATENTS

3,002,904	10/1961	Foulke et al.	204—49
3,417,005	12/1968	Baig	204—49 X

GERALD L. KAPLAN, Primary Examiner