

- [54] **ALKALINE NICKEL PLATING SOLUTIONS**
- [75] Inventors: **Arthur H. Du Rose**, Richmond Heights; **Robert L. Stern**, Cleveland Heights, both of Ohio
- [73] Assignee: **Kewanee Oil Company**, Bryn Mawr, Pa.
- [22] Filed: **June 14, 1971**
- [21] Appl. No.: **153,068**

Related U.S. Application Data

- [63] Continuation of Ser. No. 752,169, Aug. 13, 1968, abandoned.
- [52] U.S. Cl. **204/49**
- [51] Int. Cl. **C23b 5/08, C23b 5/46**

References Cited

UNITED STATES PATENTS

- 2,881,120 4/1959 Towle et al. 204/49
- 2,978,391 4/1961 DuRose 204/49
- 3,114,687 12/1963 Brandt 204/49 XR
- 3,133,006 5/1964 Ostrow et al. 204/49

- 3,417,005 12/1968 Baig 204/49 XR
- 3,428,536 2/1969 Towle et al. 204/49
- 3,485,725 12/1969 Koretzky 204/49 XR

OTHER PUBLICATIONS

Morton Schwartz, Tech. Proc. of the American Electroplaters' Soc., pp 176-183, (1960).

Primary Examiner—G. L. Kaplan
Attorney—John P. Hazzard

[57] **ABSTRACT**

An alkaline nickel electroplating bath and process wherein brighter and more ductile nickel electroplate is formed due to the inclusion of addition agents which include certain organic amines, nitriles, unsaturated organic acids and heterocyclic compounds. Such plating processes are operable from room temperature to about 180°F over a current density range of 5 to 100 amps per sq. ft. Typical addition agents include 1,6-Morpholino-2-hexyne; N-Allyl benzene sulfonamide; Sodium phosphite; Carboxymethylpyridinium iodide and 2-Phenyl-2-Cyanoethoxybutyne.

1 Claim, No Drawings

ALKALINE NICKEL PLATING SOLUTIONS

This application is a continuation of U.S. application Ser. No. 752,169 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 organic amines, nitriles, unsaturated organic acids and heterocyclic compounds. 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 percent while that for the Watts solution is -5 to +5 percent. 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) (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. 2,733,818.

Other complexing agents such as glycolic acid, tartrate, 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 no effect in alkaline nickel solutions.

Table I

1. Phenylpropionic acid (propionic 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 Pluronic

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 along (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 butyenediol at 0.2 g/l gives a bright deposit up to about 70 asf. 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'-bis-(phenylsulfonyl)-4,4'-biphenyldisulfonimide is added to an alkaline nickel solution containing butyenediol. 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 0.1 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 the 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 asf. 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 materials selected from the group consisting of acrylonitrilepolyalkalene amine; 1,6-Morpholino-2-hexyne; 5-Amino-2-benzimidazolethiol; Propiolic acid; Acetylenic substituted polyamines; β , β' -Thiodipropionitrile; Ethylenecyanohydrin; N-Allyl benzene sulfonamide; Acetylene dicarboxylic acid; Sodium phosphite; Triallyl propargyl ammonium perchlorate; Carboxymethylpyridinium iodide; 1-Diethylamino-4-acetoxy-2-butene sodium sulfonate; 2-Phenyl-2-cyanoethoxybutyne; N-Propargyl saccharin; 2-Mercaptobenzothiazole; and Acetonitrile.

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:

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	100 g/l
EDTA (Na_4) (sodium salt of ethylene diamine tetra-acetic acid)	40 g/l
Sodium Citrate	60 g/l
Ammonium Chloride	35 g/l
Triethanolamine	35 g/l
pH	8.0
Temperature	140°F

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 asf, a dull semibright deposit was obtained at 20-80 asf, a brighter deposit at 5-20 asf and a dull matte deposit at 80-100 asf. The throwing power (BSI) of the solution is 45 percent. 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

To the above solution 0.005 g/l of triallylpropargyl ammonium perchlorate was added. The deposit became brighter especially in the intermediate C. D. areas. When the brightener concentration was increased to 0.01 g/l there was a further increase in brightness so that the 70-90 asf range was semibright.

EXAMPLE 3

To solution of Example 1, 0.1 g/l of carboxymethylpyridinium chloride was added with slight brightening effect. When 0.4 g/l was used, the deposit was bright with some darkness in the low C. D. area. The addition of N,N'-bis(phenylsulfonyl)-4,4'-biphenyldisulfonimide had practically no effect. Operating without air agitation allowed the deposit to be less uniform in brightness.

EXAMPLE 4

In the solution of Example 1 N-Propargyl saccharin, 0.1 g/l effected bright and stressed deposits with air agitation. With no agitation 0.25 g/l had to be used. Addition of saccharin was of no benefit.

EXAMPLE 5

A nickel solution according to U.S. Pat. No. 2,069,566 of the following compositions was used:

$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	120 g/l
$\text{Na}_2\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$	65 "
Sodium Citrate ($2\text{H}_2\text{O}$)	60 "
Citric Acid	15 "
NaCl	30 "
NH_4OH Soln. (Sp. Gr. 88)	70 cc/l
pH	8.0
Temp. 50°C; slow air agitation	

A bent panel was plated at 20 asf average. The deposit was bright from 1 to 12 asf 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 asf, where it might be described as semibright.

EXAMPLE 6

To the same basic solution as that used in Example 5, 0.006 g/l of β , β' -thiodipropionitrile was added. This increased the bright low C. D. range only to 1 to 15 asf, but the higher C.D. areas were semibright instead of

grey. Addition of 4 percent N,N'-bis(phenylsulfonyl)-4,4'-biphenyldisulfonamide has no effect. The addition of ethoxylated butyne diol made for a fully bright deposit except that the high C. D. areas had a slight haze.

To further illustrate the difference between alkaline and acid nickel electroplating baths, two addition agents of the instant invention, namely, propiolic acid and acetylene dicarboxylic acid were added to acid nickel electroplating baths and were found to be ineffective brighteners in said 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 inven-

tion.

We claim:

1. A nickel electroplating bath comprising an aqueous alkaline solution having a pH in the range of between about 7.0 and about 11.0 and containing at least one electrolyte that yields nickel ions, said solution improved by the inclusion therein of a brightener selected from the group consisting of acrylonitrilepolyalkalene amine; 1,6-Morpholine-2-hexyne; 5-Amino-2-benzimidazoethiol; Propiolic acid; Acetylenic substituted polyamines; β , β' -Thiodipropionitrile; Ethylenecyanohydrin; N-Allyl benzene sulfonamide; Acetylene dicarboxylic acid; Triallyl propargyl ammonium perchlorate; Carboxymethylpyridinium iodide; 1-Diethylamino-4-acetoxy-2-butene sodium sulfonate; 2-Phenyl-2-cyanoethoxybutyne; N-Propargyl saccharin; 2-Mercapto-1,2,4-benzothiazole and acetonitrile.

* * * * *

20

25

30

35

40

45

50

55

60

65