

1

3,711,384

ELECTRODEPOSITION OF NICKEL

Derek Martin Lyde, 23 Red Hill, Stourbridge, England
No Drawing. Filed Jan. 20, 1971, Ser. No. 108,210

Int. Cl. C23b 5/08, 5/46

U.S. Cl. 204—49

19 Claims

ABSTRACT OF THE DISCLOSURE

An aqueous nickel plating electrolyte comprises (a) at least 30 gm. per litre of a nickel-II salt; (b) 0.1–1.0 gm. per litre of a mixture of acetylenic compounds including both an α -hydroxy-acetylenic compound and an alkylene oxide condensation product of an α -hydroxy-acetylenic compound in a weight ratio of the said condensation products to the α -hydroxy-acetylenic compounds of from 1.5:1 to 7:1; and (c) from 1.0 to 5.0 gm. per litre of saccharin or a substituted saccharin.

This invention relates to improvements in the electrodeposition of nickel, particularly to obtain bright electrodeposits.

It has long been known to employ various acetylenic compounds as organic brightening agents in nickel electroplating solutions. When an organic sulpho-oxygen compound is also present assertions have been made that a bright electrodeposit of nickel can be obtained from the solution. Thus in British patent specification No. 747,908 there is described the use as brightening additives in nickel electroplating solutions of certain acetylenic alcohols, particularly 2-butyne-1,4-diol, in combination with an organic sulpho-oxygen compound to obtain bright electrodeposits. Subsequently in British patent specification No. 864,287 the use in nickel electroplating solutions of alkynol-epoxide adducts in conjunction with an organic sulpho-oxygen compound was described as resulting in the formation of very bright nickel deposits. In both these specifications a wide variety of organic sulpho-oxygen compounds is mentioned as being suitable for use in combination with the particular acetylenic compounds specified and the use of naphthalene 1,3,6-trisulphonic acid is especially advocated.

The compositions described in the aforesaid specifications are described with particular reference to the Watt's bath, that is to an electrolyte comprising dissolved nickel-II sulphate (225–350 grams/litre), nickel-II chloride (30–50 grams/litre) and boric acid (20–45 grams/litre) and in such compositions the use of naphthalene trisulphonic acid (sodium salt) with 2-butyne-1,4-diol or with the adduct of 2-butyne-1,4-diol with two moles of alkylene oxide [often termed 1,4-di-(β -hydroxyethoxy)-2-butyne] gives satisfactorily bright nickel electrodeposits. However, when such brightening additives are employed in nickel electroplating baths of the "high chloride" type, that is containing 150–350 grams per litre of nickel-II chloride, the electrodeposits produced are unsatisfactory since they are brittle and liable to spontaneous cracking. Adjustment of the concentrations of the brightening additives fails to cure these deficiencies.

We have now discovered that very satisfactory bright and level nickel electrodeposits can be obtained from a "high chloride" nickel electroplating bath if a particular combination of acetylenic brightening agents is employed in conjunction with a minimum amount of a particular type of sulpho-oxygen compound. Moreover, such combination of additives when employed in other types of nickel-electrolyte also provide an enhanced levelling effect over those obtained by the compositions described in the aforesaid specifications. The particular acetylenic addition agents involved are a mixture containing specified

2

proportions of an α -hydroxyacetylenic compound and an alkylene oxide condensation product of such a compound and our discovery also involves the use of such mixture in conjunction with a concentration of at least 1 gram/litre of saccharin or substituted saccharin. The use of saccharin gives electrodeposits with good ductility and with little tendency to undergo spontaneous cracking.

Accordingly, the present invention provides an aqueous electrolyte for nickel plating comprising (a) at least 30 grams per litre of a nickel-II salt; (b) 0.1–1.0 gram per litre of a mixture of acetylenic compounds including both a α -hydroxy-acetylenic compound and an alkylene oxide condensation product of an α -hydroxy-acetylenic compound in a weight ratio of the said condensation products to the α -hydroxyacetylenic compounds of from 1.5:1 to 7:1; and (c) from 1.0 to 5.0 grams per litre of saccharin or a substituted saccharin.

The invention is applicable to nickel plating electrolytes which comprise at least 30 grams per litre of a nickel-II salt. Such electrolyte can be of the Watt's type which comprises 225–350 grams/litre of nickel-II sulphate, 30–50 grams/litre of nickel-II chloride and 20–45 grams/litre of boric acid. However, the invention is more particularly applicable to nickel electrolytes of the "high chloride" type which comprises 150–350 grams/litre of nickel-II chloride. Preferably such electrolytes also comprise nickel-II sulphate (50–225 g./l.), nickel-II chloride (150–200 g./l.) and boric acid (30–50 g./l.). There can also be employed electrolytes which are formed from nickel-II chloride (150–350 grams per litre) as the sole nickel salt employed and electrolytes containing other nickel salts, such as nickel-II sulphamate.

The α -hydroxyacetylenic compounds employed are compounds having a hydroxy group in an α -position to an acetylenic linkage. Preferably such compounds are α -alkynols of the general formula $R_1\text{CHOHC}\equiv R_2$ where R_1 and R_2 are each hydrogen or an alkyl, alkenyl or alkynol group of 1 to 4 carbon atoms which may optionally contain an amino or hydroxy substituent. Representative of such α -alkynols include:

2-butyne-1,4-diol;
1-butyne-3-ol;
propargyl alcohol (2-propyne-1-ol);
1-pentyne-3-ol;
4-methoxy-2-butyne-1-ol;
3-hexyne-2,5-diol;
4-diethylamino-2-butyne-1-ol; and
2,4-hexadiyne-1,6-diol.

The first three compounds of this list are especially useful.

The alkylene oxide condensation products of α -hydroxyacetylenic compounds for present use are formed by reacting an α -alkanol with from 1 to 20 moles, preferably 1–4 moles, of an alkylene oxide. The preferred alkylene oxide is ethylene oxide, but propylene oxide, epichlorohydrin or epibromohydrin may also be used. Mixtures of such alkylene oxides may also be employed, either concurrently or consecutively, in the condensation with the α -alkanol. The α -alkanol may be a compound of the formula $R_1\text{CHOHC}\equiv R_2$ as hereinbefore specified and particularly it is a member of the aforesaid list. The condensation product is formed by any of the methods usually employed for the formation of polyoxyalkylene ethers from condensation of an alcohol with an alkylene oxide. The preferred condensation products are formed from 2-butyne-1,4-diol, 1-butyne-3-ol or propargyl alcohol with about 2 moles of ethylene oxide.

The above-mentioned acetylenic compounds are employed in the electrolytes of the invention in a total con-

3

centration of 0.1 to 1.0 gram per litre. A greater weight of the α -alkynol/alkylene oxide condensation product is used over that of the simple α -alkynol, the weight ratio of condensate: α -alkynol being from 1.5:1 to 7:1. Preferably, the said ratio employed is from 2:1 to 5.5:1 since with the higher ratios there is a tendency to pitted deposits whilst with the ratio below 2.0:1 the levelling action of the additive may become impaired.

The electrolytes of the invention comprise from 1.0 to 5.0 grams of saccharin or a substituted saccharin. By "substituted saccharin" is meant an o-carboxybenzsulphimide which contains a nuclear substituent, for example an alkyl, halo- or sulpho-substituent. Nevertheless the use of saccharin itself is preferred. We find that the use of a saccharin compound is essential to obtain the improved electrodeposits with "high chloride" nickel electrolytes, particularly as regards level and ductile deposits. For present purposes a concentration of 1.5–2.5 grams per litre of saccharin is preferred.

No other sulpho-oxygen compound is essential in the electrolytes of the invention, but the presence of an additional organic sulpho-oxygen compound is often advantageous in that the electrolyte often then exhibits an increased tolerance to changes during production plating conditions. Such sulpho-oxygen compound may be any that has hitherto been advocated for use in nickel electroplating as a carrier brightener, but naphthalene 1,3,6-trisulphonic acid (added as such or as its sodium salt) is normally preferred. Other organic sulpho-oxygen compounds which may be particularly mentioned in this connection include sodium allyl sulphonate, sodium benzene sulphonate, benzene sulphonamide and p-toluenesulphonamide. Such additional organic sulpho-oxygen compound may be added in the amounts in which they are conventionally employed, e.g. from 2–20 g./l. for aromatic sulphonates and from 0.5–3 g./l. for sulphonamides.

The operating conditions for the present electrolytes are generally those normally employed for electrolytes based on the specified salts of nickel. In general the pH of the electrolyte should be between 2.5 and 5.5, a pH of 3.5–5.0 being preferred, and the temperature thereof should be 40–70° C., an operating temperature of 50–60° C. being preferred. The electrolyte may be operated under a wide range of current densities, for example at from 2–100 amps./sq. ft. and the workpiece as cathode may be agitated in the electrolyte during operation or the electrolyte may be agitated, for example by blowing air therethrough.

The nickel electrodeposits of the invention may find use as such or as the base layer on to which chromium is subsequently electrodeposited.

The invention is illustrated by the following examples.

EXAMPLE 1

To a high nickel chloride electrolyte containing nickel chloride (200 g./l.), nickel sulphate (50 g./l.) and boric acid (40 g./l.) there was added:

	G./l.
Condensate of 2-butyne-1,4-diol (1 mol.) and ethylene oxide (2 moles) -----	0.175
2-butyne-1,4-diol -----	0.089
Saccharin -----	2.5
Naphthalene trisulphonic acid (sodium salt) -----	5.0

This electrolyte having a pH of 4.5 was employed in Hull cell tests at 55° C. At current densities within the range 2 to 100 amp./sq. ft. the electrodeposit was bright and levelled. The degree of leveling at 40 amp./sq. ft. was over 70% (measured as the percentage improvement in surface roughness after depositing 0.0005 inch of nickel on to a surface of initial roughness within the range 25–30 CLA (centre line average), as defined and measured in British Standard Specification (1134). A similar degree of levelling was obtained when the naphthalenetrisulphonic acid was omitted.

4

EXAMPLE 2

Example 1 was repeated but with varying amounts of the two acetylenic compounds. The total acetylenic content was increased by up to 50% whilst keeping the ratio of condensate: α -alkynol constant. The degree of levelling remained at 70–75%, though there was a slight deterioration in the ductility of the deposit.

EXAMPLE 3

Example 1 was repeated but with the concentration of the condensate being 0.275 g./l. and that of 2-butyne-1,4-diol being 0.05 g./l. With the use of the two acetylenic compounds in this weight ratio of 5.5:1, the degree of levelling remained about 70%. There was a slight tendency for the production of pitted deposits, but this disappeared when the said ratio was reduced to 4:1.

EXAMPLE 4

An electrolyte of the Watt's type was prepared from nickel sulphate (250 g./l.), nickel chloride (50 g./l.) and boric acid (40 g./l.). Brightener additives were then included as in Example 1 and the electrolyte of pH 4.5 used in Hull cell tests at 55° C. At current densities in the range 2 to 180 amps./sq. ft. bright deposits were obtained with a degree of levelling of 70–75%.

We claim:

1. An aqueous acidic electrolyte for nickel electroplating comprising

- (a) at least 30 grams per litre of a nickel-II salt;
- (b) from 0.1–1.0 gram per litre of a mixture of acetylenic compounds including (i) an alpha-hydroxy-acetylenic compound of the formula



wherein R_1 and R_2 are each selected from hydrogen, and alkyl, alkenyl and alkynol groups having 1 to 4 carbon atoms and hydroxy substituted and amino substituted alkyl, alkenyl and alkynol groups having 1 to 4 carbon atoms; and (ii) a condensate of an alpha-hydroxy-acetylenic compound having the aforesaid formula with from 1 to 20 moles of an alkylene oxide in a weight ratio of said condensate to said alpha-hydroxy-acetylenic compound of from 1.5:1 to 7:1; and

- (c) from 1 to 5 grams per litre of saccharin or a substituted saccharin.

2. An aqueous acidic electrolyte as claimed in claim 1 which contains from 150 to 350 gms. per litre of nickel-II chloride.

3. An aqueous acidic electrolyte as claimed in claim 2 which contains from 150 to 200 gms. per litre of nickel-II chloride, from 50 to 225 gms. per litre of nickel-II sulphate and 30–50 grams per litre of boric acid.

4. An aqueous acidic electrolyte as claimed in claim 3 wherein said alpha-hydroxy acetylenic compound is selected from the group consisting of 2-butyne-1,4-diol, 1-butyne-3-ol, propargyl alcohol, 4-methoxy-2-butyne-1-ol, 3-hexyne-2,5-diol, 4-diethylamino-2-butyne-1-ol and 2,4-hexadiyne-1,6-diol, and said condensation product is a condensation product of an alpha-hydroxy acetylenic compound selected from the said group with from 1 to 20 moles of ethylene oxide.

5. An aqueous acidic electrolyte as claimed in claim 4 wherein said alpha-hydroxy acetylenic compound is 2-butyne-1,4-diol and said condensation product is a condensation product of 2-butyne-1,4-diol with from 1 to 20 moles of ethylene oxide.

6. An aqueous acidic electrolyte according to claim 5 containing from 1.5 to 2.5 gms. per litre of saccharin.

7. An aqueous acidic electrolyte as claimed in claim 6 wherein the proportion of said alpha-hydroxy acetylenic compound to said alkylene oxide condensation product is from 1:2 to 1:5.5.

5

8. An aqueous acidic electrolyte according to claim 7 wherein there is additionally present a second sulpho-oxygen compound.

9. An aqueous electrolyte according to claim 8 wherein said second sulpho-oxygen compound is naphthalene-1,3,6-trisulphonic acid.

10. An aqueous acidic electrolyte as claimed in claim 1 which is of the Watt's type and contains from 225 to 350 gms. per litre of nickel-II sulphate, from 30 to 50 gms. per litre of nickel-II chloride and from 20 to 45 gms. per litre boric acid.

11. An aqueous acidic electrolyte as claimed in claim 10 wherein said alpha-hydroxyacetylenic compound is selected from the group consisting of 2-butyne-1,4-diol, 1-butyne-3-ol and propargyl alcohol and said condensation product is a condensation product of an alpha-hydroxy acetylenic compound selected from 2-butyne-1,4-diol, 1-butyne-3-ol and propargyl alcohol with from 1 to 20 moles of ethylene oxide.

12. An aqueous acidic electrolyte as claimed in claim 11 containing 2-butyne-1,4-diol and a condensation product of 2-butyne-1,4-diol with from 1 to 20 moles ethylene oxide in a relative proportion of said 2-butyne-1,4-diol to said condensation product of from 1:2 to 1:5.5.

13. An aqueous acidic electrolyte according to claim 12 additionally containing naphthalene trisulphonic acid.

14. An aqueous acidic electrolyte as claimed in claim 1 wherein said alpha-hydroxy-acetylenic compound is selected from the group consisting of 2-butyne-1,4-diol, 1-butyne-3-ol, propargyl alcohol, 1-pentyne-3-ol, 4-methoxy-2-butyne-1-ol, 3-hexyne-2,5-diol, 4-diethylamino-2-butyne-1-ol and 2,4-hexadiyne-1,6-ol.

15. An aqueous acidic electrolyte as claimed in claim

6

14 wherein said alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide, epichlorohydrin and epibromohydrin.

16. An aqueous acidic electrolyte as claimed in claim 15 wherein the said alkylene oxide is ethylene oxide.

17. An aqueous acidic electrolyte as claimed in claim 1 wherein said alpha-hydroxy acetylenic compound is 2-butyne-1,4-diol and said condensation product of from 1 to 20 moles ethylene oxide with 2-butyne-1,4-diol.

18. An aqueous acidic electroplating electrolyte containing: about 200 gms. per litre of nickel chloride; about 50 gms. per litre nickel sulphate; about 40 gms./l. boric acid; about 0.175 gm./l. of condensate of 2-butyne-1,4-diol with about 2 moles of ethylene oxide; about 0.089 gm./l. 2-butyne-1,4-diol; about 2.5 gms./l. saccharin; and about 5.0 gms. per litre of the sodium salt of naphthalene trisulphonic acid, said electrolyte having a pH of about 4.5.

19. An aqueous acidic electroplating electrolyte containing about 250 gms./l. of nickel sulphate; about 50 gms./l. nickel chloride; about 40 gms./l. boric acid; about 0.175 gm./l. of a condensation product of 2-butyne-1,4-diol with about 2 moles ethylene oxide; about 0.089 gm./l. 2-butyne-1,4-diol; about 2.5 gms./l. saccharin and about 5.0 gms./l. of the sodium salt of naphthalene trisulphonic acid, said electrolyte having a pH of about 4.5.

References Cited

UNITED STATES PATENTS

3,366,557 1/1968 Foulke et al. ----- 204—49

GERALD L. KAPLAN, Primary Examiner