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"IMPROVED COMPOSITION AND METHOD FOR
ELECTRODEPOSITION OF BLACK NICKEL"

- A variety of processes and solutions have heretofore been used or proposed for use to deposit a dark or substantially black nickel deposit on various conductive substrates. Such so-called black nickel deposits are particularly suitable for various decorative purposes as well as to promote absorption of radiant energy such as is required in such products as solar heating systems. Typical of such prior art techniques for depositing a black coating or black nickel deposit on metallic substrates are those disclosed in United States Patents 2,679,457; 2,844,530; 3,127,279; 3,681,211 and 3,753,873.
- A continuing problem associated with such prior art techniques has been the difficulty in controlling the composition and process to consistently achieve substantially black coatings which are adherent to the substrate, which provide for improved corrosion resistance, and which are receptive to receiving a clear lacquer or other siccative finish coating.
- A recent improvement in an electrolyte composition and process for overcoming many of the problems and disadvantages associated with prior art techniques for electrodepositing dark nickel platings is disclosed in British Patent Application No. A2057505.
- It has been found in some instances, however, that the aforementioned improved electrolyte produces non-uniformity in the dark nickel deposit in high current density areas and rainbow colours and/or skip plate in the low current density areas of parts of complex

configuration when used in commercial rack plating operations.

5. The present invention provides for a still further improvement in the art of dark or black nickel plating of parts of complex configuration by providing an electrolyte and process which achieves an increase in the rate of electrodeposition over a broad range of current densities, pH, bath concentration and temperature and is adaptable for use on a variety of different
10. conductive substrates achieving consistent, substantially uniform black nickel deposits in low and, intermediate as well as high current density areas. The dark nickel deposits are further characterised by their good corrosion resistance and adhesion to the
15. metal substrate and by their receptivity to a variety of clear lacquer finish coats.

- According to the present invention a bath for depositing a substantially black nickel deposit on a substrate comprises an aqueous solution having a pH
20. ranging from 4 up to 12 and containing 2 to 25 grams per litre (g/l) nickel ions, at least 10 g/l and optionally up to bath solubility of compatible inert conductivity salts, at least 7 g/l and optionally up to bath solubility of borate ions, and a bath soluble amine
25. present in an amount to provide a mol ratio of nickel to amine in the solution of from 1:1 to 1:4, the said bath soluble amine having the formula:



Wherein:

30. n, m, and p are integers and n is 2 or 3, m is

1 or 2 or 3, and p is 2 or 3;

X represents an oxygen atom or an -NH group; and

R and R' are the same or different and represent a hydrogen atom or a $-\text{CH}_2\text{CH}=\text{CH}_2$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3$ or $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ group.

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Typical of the foregoing amines are triethylene tetramine, dipropylene triamine and 2-(2-amino ethyl-amino) ethanol.

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The operating bath may further optionally contain darkening enhancing agents comprising alkali metal salts of sulphur containing compounds such as thiocyanates, thiosulphates, bisulphites, or sulphites, which may be present in amounts up to about 25 g/l.

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The bath may optionally further contain small controlled amounts of wetting agents of the types conventionally employed in nickel electroplating solutions.

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In accordance with the method aspects of the present invention, the electroplating bath may be operated at from room temperature (70°F) (21°C) up to about 150°F (66°C) over a current density range of 2 up to 25 amperes per square foot (ASF) (0.2 to 2.75 amperes per square decimetre (ASD)). Plating times

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can vary from about 1 up to about 10 minutes depending upon bath composition and process variables.

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The novel electroplating bath of the present invention for depositing so-called black nickel deposits comprises an aqueous solution containing as its essential constituents a controlled effective amount of

- nickel ions, bath soluble inert salts to increase the conductivity of the solution, borate ions and a bath soluble amine present in a controlled amount depending upon the concentration of nickel ions present. Whilst
5. the nickel ion concentration can broadly range from about 2 g/l up to about 25 g/l, amounts ranging from about 6 to about 10 g/l are preferred. A concentration of nickel ions above about 25 g/l is undesirable in some instances in that the nickel deposit formed tends
10. to have a grey appearance at such higher concentrations. The nickel ions can be conveniently introduced into the bath in the form of bath compatible and soluble nickel salts such as nickel sulphate, nickel halide salts, nickel sulphonate, or nickel fluoborate. Of
15. the foregoing, nickel sulphate in the form of the hexahydrate comprises a preferred source. The nickel halide salts can be satisfactorily employed when a nickel anode is employed in the operating bath but are not desirable when inert anodes such as carbon anodes
20. are employed due to the evolution of the corresponding halide gas at the anode. Nickel sulphate provides a further advantage when a nickel anode is employed in that the solution does not as readily attack the surface of the anode and the build-up of nickel ion
25. concentration in the bath is substantially slower providing further simplicity in the control of the operating bath.

- A second essential constituent of the electroplating bath is a controlled amount of borate ions
30. which are present in an amount of at least about 7 g/l

- up to bath solubility with amounts of about 15 to about 30g/l being preferred. The borate ions can be introduced as boric acid as well as the bath soluble alkali metal, ammonium, and alkaline earth metal salts and mixtures thereof. Of the foregoing, boric acid itself constitutes the preferred material.
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A further essential constituent of the electroplating bath is the amine described above, which is compatible and soluble in the operating bath.

10. Typical amines suitable for use in the bath which correspond to the foregoing formula are triethylene tetramine in which R and R' are H, X is NH, and n, m and p are 2; dipropylene triamine in which R and R' are H, X is NH, m is 1 and n and p are 3; and 2-(2-amino ethylamino) ethanol in which R and R' are H, X is O, m is 1 and n and p are 2.
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- The concentration of the amine is controlled in relationship to the quantity of nickel ions present in the bath. The mol ratio of nickel ions to amine present in the solution can range from 1:1 up to 1:4, preferably 1:1.5 to 1:2.5 with ratios of about 1:2 being particularly satisfactory. Mol ratios in excess of about 1:4 are undesirable since the high concentration of amine inhibits deposition of nickel from the bath while ratios below about 1:1 do not provide a substantially black nickel deposit.
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- In addition to the nickel ions, borate ions and amine the bath further contains as an essential constituent, bath soluble compatible and inert salts to enhance the conductivity of the electrolyte. Such
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conductivity salts typically comprise alkali metal sulphates and halides as well as magnesium sulphate and magnesium halide salts. The term "alkali metal" is herein employed in its broad sense to include the

5. alkali metals sodium, potassium and lithium as well as the ammonium ion.

Such conductivity salts or mixtures thereof are employed in amounts of at least 10 g/l up to the solubility limit thereof with amounts ranging from 30

10. up to 50 g/l being preferred. Sodium sulphate in combination with boric acid affords a particularly satisfactory bath composition.

In addition to the foregoing, the bath may further contain as an optional constituent, a darkening enhancing agent which is present in controlled amounts so as

15. to further enhance the darkness or black finish of the deposit. Darkening enhancing agents suitable for use are alkali metal salts of sulphur containing compounds including thiocyanates, thiosulphates, bisulphites, and

20. sulphites, as well as mixtures thereof. When used, such darkening enhancing agents can be employed in amounts up to about 25 g/l while amounts of 1 to 5 g/l are usually preferred. Normally, concentrations of such darkening enhancing agents above about 25 g/l are

25. undesirable due to the degradation products formed by the use of such high concentrations which in some instances impair the uniformity and coverage of the black nickel deposit. In addition, no particular benefits are achieved by employing such agents in

30. amounts greater than 25 g/l in comparison to that

obtained when using lesser amounts such as about 5 g/l.

- As a further optional constituent, the electroplating bath can incorporate effective amounts of any one of a variety of bath compatible wetting agents of the various types conventionally employed in nickel plating solutions. Normally, wetting agents of the anionic type are employed in concentrations up to about 200 mg/l while amounts of 50 to 100 mg/l are preferred. Typical of suitable wetting agents that can be employed are sulphates of primary alcohols containing 8 to 18 carbon atoms such as sodium lauryl sulphate, and sodium lauryl ethoxy sulphates or sulphonates.

- In accordance with the process aspects of the present invention, the operating bath temperature can range from room temperature (70°F) (21°C) up to 150°F (66°C) with temperatures of from 80°F (27°C) to 90°F (32°C) being particularly preferred from an energy conservation standpoint. The particular temperature best employed to achieve optimum black nickel deposits will vary depending upon the specific composition and operating conditions employed.

- The aqueous operating bath is controlled so as to have a pH in the range of 4 up to 12 and a pH range of 6 to 10 is preferred. Adjustment of the pH can be achieved by employing acids such as sulphuric acid or hydrochloric acid, or employing bases such as alkali metal hydroxides including ammonium hydroxide.

- The electrodeposition of the black nickel deposit can be carried out using an average current density ranging from as low as about 2 up to about 25 ASF (0.2

to 2.75 ASD). Preferably, the current density is controlled so as to be within the range of about 5 to about 15 ASF (0.5 to 1.65 ASD).

5. The time for which plating is carried out can broadly range from as low as about 1 minute up to about 10 minutes depending upon the particular bath composition used, the type of the substrate employed, the type of finish desired and the specific current density used. Normally, plating times ranging from about 2 to 10. about 3 minutes are satisfactory.

15. The electrodeposition of the black nickel coating can be satisfactorily achieved on conductive metal substrates, including nickel, copper, brass, electrodeposited zinc, and cadmium. In order to achieve a lustrous bright, substantially black nickel deposit, it is preferred that the substrate be in a bright condition either by depositing a bright electrodeposit on the surface or by mechanical means such as buffing. As the substrate becomes less bright, then the resultant 20. nickel deposit tends progressively to become greyer.

The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples.

25. EXAMPLE 1A

30. An electroplating solution was prepared consisting of 17 g/l of nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), 14 g/l of 2(2-aminoethylamino) ethanol, 5 g/l sodium thiocyanate (NaCNS), 37.5 g/l of sodium sulphate (Na_2SO_4), and 0.2 g/l of an anionic wetting agent. The

- pH was adjusted to 6 with sulphuric acid (H_2SO_4). A work rack carrying a plurality of household plumbing fixtures of complex shape was immersed into the solution and plated for 2 to 3 minutes at 10 ASF (1.1 ASD) and 75°F (24°C). The deposit was satisfactory on the high and intermediate current density areas of the workpieces but was of an unsatisfactory rainbow appearance in the low current density deep recess areas.

EXAMPLE 1B

- In an effort to overcome the problem of Example 1A, that example was repeated but the average current density of the electroplating operation was increased to 15 ASF (1.65 ASD) and a second rack of the same workpieces was plated. This time, an improvement of the deposit in the low current density areas was obtained but a dull grey cloudiness was present in the deposit on the high current density areas.

EXAMPLE 2A

- An electroplating solution was prepared as in Example 1A but with the addition of 22.5 g/l of boric acid. A work rack containing the same workpieces as in Example 1A was immersed in the solution and plated for 2 to 3 minutes at 10 ASF (1.1 ASD) and 75°F (24°C). The deposit was uniformly black with good adhesion over the entire surface including the low current density deep recess areas.

EXAMPLE 2B

- A second work rack of fresh workpieces was plated in the solution of Example 2A under the same conditions used therein but at an average current density of

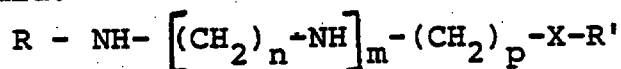
15 ASF (1.65 ASD). Again, the deposit was uniformly black with good adhesion and good black colour including the high current density areas.

- 5. The use of the borate ions and conductivity salts also permits electrodeposition of uniform black nickel deposits in less time because of the increased throwing power of the bath and its improved plating characteristics.



CLAIMS

1. A bath for electrodepositing a black nickel deposit on a substrate comprising an aqueous solution having a pH of 4 to 12 and containing 2 to 25 g/l of nickel ions, at least 7 g/l of borate ions, at least 10 g/l of bath soluble and compatible inert conductivity salts and a bath soluble amine present in an amount to provide a mol ratio of nickel to amine in the solution of 1:1 to 1:4, the said amine having the formula:



wherein:

n, m and p are integers and n is 2 or 3, m is 1 or 2 or 3, and p is 2 or 3;

X represents an oxygen atom or an -NH group; and

R and R' are the same or different and represent a hydrogen atom or a $-CH_2CH = CH_2$, $-CH_2CH_2CH_2SO_3$ or $-CH_2CHCH_2OH$ group.

OH

2. A bath as claimed in Claim 1 in which the said nickel ions are present in an amount of 6 to 10 g/l.

3. A bath as claimed in Claim 1 or Claim 2 in which the said amine is present to provide a mol ratio of nickel to amine of 1:1.5 to 1:2.5.

4. A bath as claimed in Claim 3 in which the said amine is present to provide a mole ratio of nickel to amine of about 1:2.

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5. A bath as claimed in any one of Claims 1 to 4 in which the said borate ions are present in an amount of 7 g/l up to their solubility limit in the bath.

6. A bath as claimed in Claim 5 in which the said borate ions are present in an amount of 15 to 30 g/l.

7. A bath as claimed in any one of Claims 1 to 6 in which the said conductivity salts are present in an amount of 10 g/l up to their solubility limit in the bath.

8. A bath as claimed in Claim 7 in which the said conductivity salts are present in an amount of 30 to 50 g/l.

9. A bath as claimed in any one of Claims 1 to 8 in which the said conductivity salts comprise an alkali metal or ammonium sulphate, an alkali metal or ammonium halide, magnesium sulphate, or a magnesium halide or mixtures thereof.

10. A bath as claimed in any one of Claims 1 to 9 in which the said borate ions are present in an amount of 15 to 30 g/l and the said conductivity salts are present in an amount of 30 to 50 g/l.

11. A bath as claimed in any one of Claims 1 to 10 in which the said borate ions are present as boric acid



in an amount of 15 to 30 g/l and the said conductivity salts consist of or include sodium sulphate in an amount of 30 to 50 g/l.

12. A bath as claimed in any one of Claims 1 to 11 further including as a darkening enhancing agent an alkali metal sulphur compound comprising a thiocyanate, a thiosulphate, a bisulphite, or a sulphite, or mixtures thereof, present in an amount up to 25 g/l.

13. A bath as claimed in Claim 12 in which the said darkening enhancing agent is present in an amount of 1 to 5 g/l.

14. A bath as claimed in any one of Claims 1 to 13 further including up to 200 mg/l of a bath compatible wetting agent.

15. A bath as claimed in Claim 14 in which the said wetting agent comprises an anionic wetting agent and is present in an amount of 50 to 100 mg/l.

16. A bath as claimed in any one of Claims 1 to 15 in which the said amine comprises triethylene tetramine, dipropylene triamine, 2-(2-amino ethylamino) ethanol, or a mixture thereof.

17. A bath as claimed in Claim 1 substantially as specifically described herein with reference to Example 2A.



18. A method for electrodepositing a substantially black nickel deposit on a substrate which comprises the steps of electrodepositing nickel at a current density of 2 to 25 ASF (0.2 to 2.75 ASD) for a period of time sufficient to deposit the desired thickness of deposit from a plating bath as claimed in any one of Claims 1 to 17 at a temperature of from room temperature up to 150°F (66°C).

19. A method as claimed in Claim 18 substantially as specifically described herein with reference to Example 2A or 2B.

20. An article whenever provided with a substantially black nickel deposit by a method as claimed in Claim 18 or Claim 19.

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