

COMPOSITION AND METHOD FOR ELECTRO-
DEPOSITION OF BLACK NICKEL

The present invention relates to solutions and processes using the solutions for plating black nickel deposits.

5. 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.
10. of radiant energy such as in 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 2,679,475; 2,844,530; 3,127,279; 3,681,211
15. and 3,753,873.

- A continuing problem associated with such prior art techniques has been the difficulty in controlling the bath composition and process to consistently achieve substantially black coatings which are
20. adherent to the substrate, which provide for improved corrosion resistance, and which are receptive to receiving a clear lacquer or other siccative finish coating.

- The problems and disadvantages associated with
25. known prior art techniques are reduced or overcome in accordance with the composition and method of the present invention. The bath composition can be

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- operated over a broad range of pH, concentration, current density and temperature, and is capable of being used on a variety of different conductive substrates to produce consistently substantially uniform and adherent substantially black nickel deposits which provide improved corrosion resistance and are also receptive to a variety of clear lacquer finish coats.
5. uniform and adherent substantially black nickel deposits which provide improved corrosion resistance and are also receptive to a variety of clear lacquer finish coats.

- According to the present invention a plating bath for plating black nickel deposits comprises an aqueous solution having a pH ranging from 4 up to 12 and containing as its essential constituents, 2 to 25 grams per litre (g/l) of nickel ions in combination with a bath soluble amine present in an amount to provide a mol ratio of nickel to amine in the solution of from 1:1 to 1:4. Suitable bath soluble amines are of the formula:
10. for plating black nickel deposits comprises an aqueous solution having a pH ranging from 4 up to 12 and containing as its essential constituents, 2 to 25 grams per litre (g/l) of nickel ions in combination with a bath soluble amine present in an amount to provide a mol ratio of nickel to amine in the solution of from 1:1 to 1:4. Suitable bath soluble amines are of the formula:
15. mol ratio of nickel to amine in the solution of from 1:1 to 1:4. Suitable bath soluble amines are of the formula:



20.

wherein:

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

X represents an oxygen atom or an NH group; and

25. 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

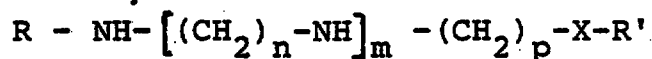
Typical of the foregoing amines are triethylene tetramine, dipropylene triamine and 2-(2-amino ethylamino) ethanol.

5. 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. Optionally the bath may further contain bath
10. soluble inert salts to increase the conductivity thereof as well as small controlled amounts of wetting agents of the types conventionally employed in nickel electroplating solutions.

15. In accordance with the method 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). (0.22 to 2.75 amperes per square decimetre (ASD)). Plating times can vary from 1 up to
20. 10 minutes depending upon bath composition and process variables.

25. 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 in combination with a bath soluble amine present in a controlled amount depending upon the concentration of nickel ions present. The nickel ion concentration may be in the range from 2 g/l up to 25
30. g/l with amounts in the range from 6 to 10 g/l being preferred. A concentration of nickel ions above about

- 25 g/l is undesirable in some instances because the nickel deposit formed tends to have a grey appearance at such concentrations. The nickel ions may be 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 the foregoing, nickel sulphate in the form of the hexahydrate is preferred. 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 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 concentration in the bath is substantially slower providing further simplicity in the control of the operating bath.
20. The second essential constituent of the electroplating bath is an amine which is compatible and soluble in the operating bath and has the formula:



25.

wherein:

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

X represents an oxygen atom or an NH group; and

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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 $-\text{CH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{OH}$ group.

5. 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.

15. 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 is in the 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.

20. In addition to the nickel ions and amine as essential bath constituents, the bath may further contain as an optional constituent, bath soluble compatible and inert salts to enhance the conductivity of the electrolyte. Such conductivity salts typically comprise alkali metal sulphates and halides as well as magnesium sulphate and magnesium halide salts. The term "alkali metal" is employed in its broad sense to include the alkali metals sodium, potassium, and lithium as well as ammonium.

Such conductivity salts or mixtures thereof can be employed in amounts up to the solubility limit thereof with amounts ranging from 30 up to 50 g/l being preferred.

5. A further optional constituent of the bath comprises a darkening enhancing agent which is present in controlled amounts so as 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 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 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.
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20. In addition, no particular benefits are achieved by employing such agents in 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 an effective amount 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
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preferred. Typical examples 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.

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In accordance with the method of the present invention, the operating bath temperature can range from room temperature (70°F) (21°C) up to about 150°F (66°C) with temperatures of from 80°F to 90°F (27°C to 32°C) being particularly preferred from an energy conservation standpoint.

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The particular temperature employed will vary to achieve optimum black nickel deposits depending upon the specific composition and operating conditions employed.

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The aqueous operating bath is controlled to have a pH in the range of 4 up to 12 while 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 a base such as an alkali metal hydroxide or ammonium hydroxide.

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The electrodeposition of the black nickel deposit can be achieved using an average current density ranging from 2 up to 25 ASF. (0.22 up to 2.75 ASD). Preferably, the current density is controlled within a range of 5 to 15 ASF (0.55 to 1.65 ASD).

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The duration of the plating process can range from 1 up to 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 2 to 3 minutes are satisfactory.

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- The black nickel coating can be deposited 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. The less bright is the substrate the greyer is the resultant nickel deposit likely to be.
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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.

15.

EXAMPLE I

- An electroplating solution is made up consisting of 26 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 26 g/l of triethylene tetramine. The pH of the solution is adjusted to 12 with sodium hydroxide. A freshly prepared bright nickel plated work piece is immersed into the solution and connected to the cathode pole of a power source. Carbon rods are connected to the anode pole of the power source to complete the circuit. The work piece is plated for 2 - 3 minutes at 15 ASF (1.65 ASD) at 75°F (24°C). The deposit is uniformly black with good adhesion.
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EXAMPLE II

- An electroplating solution is made up consisting of 26 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 26 g/l of dipropylene tri-amine. The pH of the solution is adjusted to 4 with
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sulphuric acid. A freshly prepared bright nickel plated work piece is immersed into the solution and plated for 2 to 3 minutes at 15 ASF (1.65 ASD) and 75°F. The deposit is uniformly black with good adhesion.

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EXAMPLE III

An electroplating solution is made up consisting of 26 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and 21 g/l of 2-(2-aminoethylamino) ethanol. The pH of the solution is adjusted to 12 with sodium hydroxide. A freshly prepared bright nickel plated work piece is immersed into the solution and plated for 2 to 3 minutes at 15 ASF (1.65 ASD) and 75°F (24°C). The deposit is uniformly black with good adhesion.

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EXAMPLE IV

15. An electroplating solution is made up consisting of 26 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 21 g/l of 2-(2-aminoethylamino) ethanol and 5 g/l of sodium thiocyanate (NaCNS). The pH of the solution is adjusted to 12 with sodium hydroxide. A freshly prepared bright nickel plated work piece is immersed into the solution and plated for 2 to 3 minutes at 15 ASF (1.65 ASD) and 75°F (24°C). The deposit is uniformly black with good adhesion.

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EXAMPLE V

25. An electroplating solution is made up consisting of 26 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 21 g/l of 2-(2-aminoethylamino) ethanol and 10 g/l of sodium bisulphite ($\text{Na}_2\text{S}_2\text{O}_3$). The pH of the solution is adjusted to 12 with sodium hydroxide. A freshly prepared nickel work piece is immersed into the solution and plated for 2 to 3 minutes at 15 ASF (1.65 ASD) and 75°F (24°C). The deposit is uniformly black with good adhesion.

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5. The addition of either sodium thiocyanate or sodium thiosulphate to the electroplating solution of Examples IV and V serve as a darkening enhancing agent and the nickel deposits obtained in Examples IV and V are much darker than that obtained with the identical solution of Example III but devoid of any darkening enhancing agent.

EXAMPLE VI

10. An electroplating solution is prepared, consisting of 25 g/l Ni $(\text{NH}_2\text{SO}_3)_2$, 21 g/l 2-(2-aminoethylamino) ethanol and 5 g/l of sodium thiocyanate (NaCNS). The pH is adjusted to 6 with sulphuric acid. A freshly prepared nickel work piece is immersed into the solution and plated for 2 to 3 minutes at 10 ASF (0.11 ASD) and 75°F (24°C). The deposit is uniformly black with good
15. adhesion.

EXAMPLE VII

20. An electroplating solution is prepared consisting of 23 g/l nickel fluoroborate $(\text{Ni}(\text{BF}_4)_2)$, 21 g/l of 2-(2-aminoethylamino) ethanol and 5 g/l sodium thiocyanate (NaCNS). The pH is adjusted to 6 with sulphuric acid. A freshly prepared nickel work piece is immersed into the solution and plated for 2 to 3 minutes at 10 ASF (0.11 ASD) and 75°F (24°C). The deposit is uniformly
30. black with good adhesion.

EXAMPLE VIII

35. An electroplating solution is prepared consisting of 24 g/l of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 21 g/l of 2-(2-aminoethylamino) ethanol and 5 g/l sodium thiocyanate (NaCNS). The pH is adjusted to 6 with sulphuric acid. A freshly prepared nickel work piece is immersed into the solution and plated for 2 to 3 minutes at 10 ASF (0.11 ASD) and 75°F (24°C). The deposit is uniformly black with good adhesion.

EXAMPLE IX

- An electroplating solution is prepared consisting of 17 g/l of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 14 g/l of 2-(2-aminoethyl-amino) ethanol, 5 g/l sodium thiocyanate (NaCNS), 40 g/l of sodium sulphate (Na_2SO_4) and 0.2 g/l of an anionic wetting agent, sodium lauryl sulphate. The pH is adjusted to 6 with sulphuric acid. A freshly prepared nickel work piece is immersed into the solution and plated for 2 to 3 minutes at 10 ASF (0.11 ASD) and 75°C (24°C). The deposit is uniformly black with good adhesion.

EXAMPLE X

- An electroplating solution is prepared consisting of 40 g/l of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 33 g/l of 2-(2-aminoethyl-amino) ethanol, 5 g/l sodium thiocyanate (NaCNS), 30 g/l of sodium sulphate (Na_2SO_4) and 0.1 g/l of an anionic wetting agent, sodium lauryl ethoxy sulphate. The pH is adjusted to 6 with sulphuric acid. A freshly prepared nickel work piece is immersed into the solution and plated for 2 to 3 minutes at 10ASF (0.11 ASD) and 75°F (24°C). The deposit is uniformly black with good adhesion.

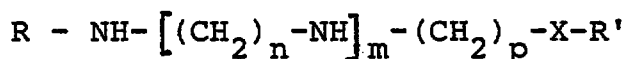
EXAMPLE XI

- An electroplating solution is prepared consisting of 26 g/l $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, 21 g/l of 2-(2-aminoethylamino) ethanol, 5 g/l sodium thiocyanate (NaCNS), 40 g/l of sodium sulphate (Na_2SO_4) and 0.2 g/l of sodium lauryl sulphate. The pH is adjusted to 6 with sulphuric acid. A freshly prepared nickel work piece is immersed into the solution and plated for 2 to 3 minutes at 10 ASF (0.11 ASD) and 150°F (66°C). The deposit is black with good adhesion.



CLAIMS

1. A bath for electrodepositing a substantially 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, 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 corresponding to the formula:



wherein:

n, m and p are integers and n is 2 or 3, m is 1, 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 $-CH_2CH = CH_2$, $-CH_2CH_2CH_2SO_3$ or $-CH_2\underset{\substack{| \\ OH}}{CH}CH_2OH$ group.

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 in an amount such as to provide a mol ratio of nickel to amine of 1:1.5 to 1:2.5.



4. A bath as claimed in Claim 1 or Claim 2 in which the said amine is present in an amount such as to provide a mol ratio of nickel to amine of about 1:2.

5. A bath as claimed in any one of Claims 1 to 4 including bath soluble and compatible inert conductivity salts present in an amount up to their solubility limit in the bath.

6. A bath as claimed in Claim 5 in which the bath soluble and compatible inert conductivity salts are selected from alkali metal sulphates, alkali metal halides, magnesium sulphate, magnesium halides and mixtures thereof.

7. A bath as claimed in Claim 6 in which the conductivity salts are present in an amount of 30 to 50 g/l.

8. A bath as claimed in any one of Claims 1 to 7 further including as a darkening enhancing agent an alkali metal thiocyanate, thiosulphate, bisulphite, sulphite or mixture thereof.

9. A bath as claimed in Claim 7 in which the darkening enhancing agent is present in an amount up to about 25 g/l.

10. A bath as claimed in Claim 9 in which the said darkening enhancing agent is present in an amount of 1 to 5 g/l.



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11. A bath as claimed in any one of Claims 1 to 10 further including up to about 200 mg/l of a bath compatible wetting agent.

12. A bath as claimed in Claim 11 in which the said wetting agent is an anionic wetting agent.

13. A bath as claimed in Claim 12 in which the wetting agent is present in an amount of 50 to 100 mg/l.

14. A bath as claimed in any one of Claims 1 to 13 in which the amine is triethylene tetramine, di-propylene triamine, 2-(2- aminoethylamino) ethanol, or a mixture thereof.

15. A bath as claimed in Claim 1 substantially as specifically described herein with reference to any one of the Examples.

16. 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 (0.22 to 2.75 ASD) for a period of time sufficient to deposit the desired thickness of deposit from an aqueous solution as defined in any one of Claims 1 to 15 at a temperature from room temperature up to 150°F (66°C).

17. A method as claimed in Claim 16 substantially as specifically described herein with reference to any one of the Examples.

18. A substrate whenever provided with a deposit by a method as claimed in Claim 16 or Claim 17.