

Description

The present invention concerns a thallium free electroless nickel - boron plating composition and a process of electroless plating a thallium free nickel - boron coating onto a substrate material.

Electroless nickel-boron plating compositions are known to supply hard, wear resistant coatings to various wear sensitive substrates. Because of recent environmental concerns the toxicity of electroless plating compositions has been looked at more closely. Current commercial processes use such materials as thallium to stabilize the plating compositions. However, thallium containing compositions do present some disposal problems because of their toxicity. On the other hand, the use of thallium in such plating compositions does provide good wear resistant properties.

There are compositions which are known which use thiourea in place of thallium. This does address some of the toxicity problems. And while the thiourea containing compositions do provide coatings with properties comparable to the use of thallium containing compositions, there is a constant search in this art for compositions which will provide improved coatings, such as improved wear resistance.

The thallium free electroless nickel-boron plating solution of the present invention comprises water, a water soluble nickel salt, a chelating agent, alkali metal hydroxide, a boron containing reducing agent and 0.098×10^{-5} mole per litre to 9.8×10^{-5} mole per litre of ethylenethiourea.

An electroless nickel-boron coating solution is disclosed comprising an alkali metal hydroxide, a water soluble nickel salt, a chelating agent, a boron containing reducing agent and ethylenethiourea. The composition, in addition to being thallium free, results in improved luster, density, and wear resistance over other compositions.

Another aspect of the invention is a process for coating substrate materials with the above composition.

The process of the present invention comprises immersing the substrate in an aqueous solution comprising water, a water soluble nickel salt, a chelating agent, alkali metal hydroxide, a boron containing reducing agent and 0.098×10^{-5} mole per litre to 9.8×10^{-5} mole per litre of ethylenethiourea, said solution being heated to a temperature of 85°C to 102°C (185°F to 215°F), and removing the substrate from the solution, resulting in a nickel boron coated substrate having improved wear resistance.

A solution of the nickel salt, chelating agent and alkali metal hydroxide, are heated together to a temperature of 85°C to 102°C (185°F to 215°F). Following the heating step the ethylenethiourea and boron containing reducing components are added to initiate plating in the presence of the parts. The parts to be

plated are then immersed in the solution. The concentrations of the nickel salt, boron containing reducing agent, ethylenethiourea, and alkali metal hydroxide (pH) are maintained over the entire plating period. Upon removal from the bath the parts have a nickel boron coating with improved wear resistance.

The foregoing and other features and advantages of the present invention will become more apparent from the following description.

The alkali metal hydroxide preferred for use in the coating composition of the present invention is typically either sodium or potassium hydroxide. This material is used in amounts sufficient to produce a pH of 12 to 14, preferably about 13 to 14, and most preferably 13.7 to 14. The alkali metal hydroxide helps to maintain bath stability e.g. by keeping the borohydride stable and keeping the substrate material active (for plating and coating adherence) throughout the deposition process.

The nickel in the bath is provided through the use of a water soluble nickel salt. Nickel sulfamate is the preferred nickel salt. Other nickel compounds which may be used are nickel chloride, nickel sulfate, nickel ammonium sulfate, nickel acetate, nickel formate, and other water soluble nickel salts. Preferably the nickel component is present in an amount of 0.09 mole per liter although concentrations of 0.01 to 0.15 mole per liter can be used.

The amount of the nickel salt used in the bath is strongly dependent upon the concentration of chelating agent present in the bath. The preferred chelating agent is ethylenediamine. Other chelating agents which may be used are diethylenetriamine, triethylenetetraamine, ethylenediaminetetraacetate, diethylenetriaminepentaacetate. The amount of chelating agent used in the bath is determined by the amount of nickel present in the bath. Typically the molar concentration ratio of chelating agent to nickel is (in moles) 4/1 to 12/1, preferably 7/1 to 9/1, and most preferably 8/1 to 8.5/1 with 8.25/1 being the target. These ratios, and the concentrations of all of the active components can be monitored utilizing conventional chromatography and titrimetry techniques.

The boron containing reducing agent provides electrons to the catalytic surfaces to reduce the complexed nickel cations in the bath and also provides the boron content of the coating. The preferred boron compound is sodium borohydride and other boron compounds which may be used include potassium borohydride, tetralkyl ammonium borohydride, alkylamine boranes, and tetraphenyl phosphonium borohydride. The borohydride component is typically used in a concentration of 0.002 mole to 0.052 mole per liter preferably 0.002 mole to 0.026 mole per liter, and most preferably at a concentration of 0.010 mole per liter.

The ethylenethiourea component serves a bath stabilizing function. It is present in an amount of 0.1

ppm (parts per million) to 10 ppm (0.098 to 9.8, $\times 10^{-5}$ mole per liter), preferably 0.5 ppm to 4 ppm (0.49 to 3.9, $\times 10^{-5}$ mole per liter), and most preferably 0.7 ppm to 2.5 ppm (0.6873 to 2.455, $\times 10^{-5}$ mole per liter).

The solution of the present invention is typically made by admixing the nickel salt, chelating agent and alkali metal hydroxide. The solution is then heated to a temperature of 85°C to 102°C (185°F to 215°F). The ethylenethiourea and boron containing reducing agent are next added. The parts to be plated are then immersed in the plating solution and the concentrations of the components, pH and temperature maintained stable over the coating period. Functionally the temperature must not be so low that the nickel will not plate and not so high that the solution becomes unstable resulting in the precipitation of nickel boride particles. Typically temperatures of 88°C to 99°C (190°F to 210°F) are usable, with 89°C to 92°C (193°F to 197°F) preferred and 90°C to 91°C (195°F to 196°F) most preferred.

The plating rate varies between 0.025 and 0.012 mm (0.0001 and 0.0005 inch) of thickness per hour depending on the maintenance of the concentration of components, especially the boron reducing agent, ethylenethiourea component and the temperature maintained. Typically what is aimed for is a coating to 19.0 to 38.1 μm (0.75 to 1.5 mils) thick coating of nickel boride. Flash coatings have been applied, and coatings as high as 127 μm (5 mils) have also been produced. In fact, another advantage of the composition and process of the present invention is that low internal stresses are produced in the plate, allowing greater thicknesses to be deposited without exceeding the adhesive strength of the plate to the substrate. This allows plating to even greater plate thicknesses (for example, up to 1270 μm (50 mils). Coatings as low as 2.54 μm (0.1 mil) are considered acceptable for some alloys (e.g. copper) alloys. The problem with thinner coatings is that during heat treatment, the boron tends to diffuse into the substrate which reduces the amount available for the nickel boride formation, which would result in less wear resistance.

If the concentration of the components remains constant, the thickness would be determined by the amount of time the substrate spends in the bath, also depending upon the temperature range maintained. And while any metal substrate can be coated with the process of the present invention, it is particularly well suited for titanium, steel, nickel, and copper (of course it is understood that while the substrate material is recited in terms of the metal material, this is meant to include the alloys of such metals as well). Other metals such as magnesium and aluminum can be coated if they are first subjected to a flash or strike coating (for example, zincate type immersion plate, followed by copper strike, and optionally a nickel strike coating) to protect the metal from attack at the high pH values

used. The process is particularly well suited to substrate material which is prone to galling. The advantage to lighter weight metals such as titanium, aluminum and magnesium is that they can be provided with improved wear resistance by the process of the present invention. Gas turbine engine parts are particularly well suited for coating by the process of the present invention. It should be noted that the plating composition can also be applied to plastic substrate material (such as polyimides, acrylates, nylon, polyethylene, polypropylene, etc.). This would require a pre-treatment of the plastic substrate material with a sensitizing solution to make the plastic catalytic. By making the surface catalytic this allows electrons to be transferred from the reducing agent to the plastic surface and transferred again from the plastic surface to reduce the nickel. Treatment of the surface of the plastic substrate material with tin chloride solutions followed by subsequent treatment with solutions of palladium chloride are conventional sensitizing treatments in this art.

EXAMPLE

36 liters of high purity water was mixed with 2.8 liters of ethylenediamine. 1.74 kilograms of nickel sulfamate tetrahydrate and 2.6 kilograms of sodium hydroxide were added to this solution followed by the addition of sufficient water to yield 56 liters of solution (solution A). 0.1022 grams of ethylenethiourea were dissolved in sufficient water to yield 4 liters of solution (solution B). 800 grams of sodium hydroxide and 160 grams of sodium borohydride were dissolved in sufficient water to yield 4 liters of solution (solution C). 320 grams of nickel sulfamate, 300 milliliters of ethylenediamine, and 10 grams of sodium hydroxide were dissolved in sufficient water to yield 2 liters of solution (solution D).

Solution A was prepared in a 57 l (15 gallon) polypropylene and polytetrafluoroethylene plating rig fitted with a circulating pump and filter system. A polytetrafluoroethylene encapsulated immersion heater and temperature sensor was used to control the solution temperature $90^{\circ}\text{C} \pm 1^{\circ}\text{C}$ at ($195^{\circ}\text{F} \pm 2^{\circ}\text{F}$). Solutions B, C and D were continually added from separate reservoirs by magnetically coupled, variable gear pumps based on analyses provided by ion and high performance liquid chromatography. The pH was maintained at 13.7 (or higher) by periodic additions of strong (5 molar) sodium hydroxide solution.

5 AMS 5508 (Greek ASCOLOY) panel measuring 516 cm^2 (80 square inches) total and 3 Inconel 718 wear specimens measuring 6.45 cm^2 (14 square inches) total were vapor blasted, activated in a 50 volume percent hydrochloric acid solution, flash nickel plated in a hydrochloric acid nickel chloride solution, rinsed, and transferred to the nickel-boron plating solution. During the course of plating, the solution

chemistry was maintained as follows: nickel cation (Ni^{+2}) 5600 ppm to 6400 ppm (0.095 to 0.109 mole per liter nickel sulfamate tetrahydrate); ethylenediamine, 47000 to 53000 ppm (0.782 to 0.883 mole per liter); borohydride anion (BH_4^{-1}) 125 to 177 ppm (8.46 to 11.90, $\times 10^{-3}$ mole per liter sodium borohydride); ethylenethiourea, 1.1 to 1.6 ppm (1.08 to 1.57, $\times 10^{-6}$ mole per liter).

Plating of the specimens was maintained over a 9 hour period after which the parts were rinsed, dried and heat treated for 90 minutes at 357°C (675°F). The resulting nickel-boron plating measured 0.05 mm (0.002 inch) in thickness with a minimum hardness of 1000 HV (Hardness, Vickers). As plated, the coating consists of an amorphous layer of nickel and boron. Subsequent heat treatment yields a fine dispersion of nickel boride particles in a nickel matrix resulting in improved wear resistance over the coating if it is not heat treated.

The plating bath is ideally operated utilizing an automated analysis/solution replenishment system. Such a system would incorporate a computer controlled solution replenishment feedback system with the high performance liquid and ion chromatography.

In addition to the improved luster resulting from the present process, higher density and improved wear resistance are also produced in the coated articles according to the present invention. It is also significant to note that the composition is thallium free. The elimination of the thallium in the solution produces a significant reduction in toxicity hazard for the platers. It should also be noted that being thallium free the plating solution is easier to handle in terms of hazardous waste and disposal.

Claims

1. A thallium free electroless nickel-boron plating solution comprising water, a water soluble nickel salt, a chelating agent, alkali metal hydroxide, a boron containing reducing agent and 0.098×10^{-5} mole per litre to 9.8×10^{-5} mole per litre of ethylenethiourea.

2. The solution of claim 1 wherein the alkali metal hydroxide is sodium or potassium hydroxide present in an amount sufficient to produce a pH of 12 to 14.

3. The solution of claim 1 wherein the water soluble nickel salt is nickel sulfamate present in an amount of 0.01 mole per liter to 0.15 mole per liter.

4. The solution of claim 1 wherein the chelating agent is ethylenediamine and the molar concentration ratio of chelating agent to nickel salt is 4/1 to 12/1.

5. The solution of claim 1 wherein the ethylenethiourea is present in an amount of 0.49×10^{-5} to 3.9×10^{-5} mole per liter.

6. The solution of claim 1 wherein the boron containing reducing agent is sodium borohydride present in an amount of 0.002 mole per liter to 0.052 mole per

liter.

7. A process of electroless plating a thallium free nickel-boron, coating onto a substrate material which comprises immersing the substrate in an aqueous solution comprising water, a water soluble nickel salt, a chelating agent, an alkali metal hydroxide, a boron containing reducing agent and 0.098×10^{-5} mole per litre to 9.8×10^{-5} mole per litre of ethylenethiourea, said solution being heated to a temperature of 85°C to 102°C (185°F to 215°F), and removing the substrate from the solution, resulting in a nickel boron coated substrate having improved wear resistance.

8. The process of claim 7 including maintaining concentrations of the solution components and the solution temperature constant throughout the plating process.

9. The process of claim 7 wherein the alkali metal hydroxide is sodium or potassium hydroxide present in an amount sufficient to produce a pH of 12 to 14.

10. The process of claim 7 wherein the water soluble nickel salt is nickel sulfamate present in an amount of 0.01 mole per liter to 0.15 mole per liter.

11. The process of claim 7 wherein the chelating agent is ethylenediamine and the molar concentration ratio of chelating agent to nickel salt is 4/1 to 12/1.

12. The process of claim 7 wherein the ethylenethiourea is present in an amount of 0.49×10^{-5} to 3.9×10^{-5} mole per liter.

13. The process of claim 7 wherein the substrate comprises titanium, steel, nickel, copper, aluminum or magnesium.

14. The process of claim 7 wherein the coating is at least $2.54 \mu\text{m}$ (0.1 mil) thick.

Patentansprüche

1. Thalliumfreie Lösung zum stromlosen Nickel-Bor-Auftragen, die aus Wasser, einem wasserlöslichen Nickelsalz, einem chelatbildenden Mittel, einem Alkalimetallhydroxid, einem Bor enthaltenden Reduktionsmittel und $0,098 \times 10^{-5}$ Mol pro Liter bis $9,8 \times 10^{-5}$ Mol pro Liter Ethylenethioharnstoff besteht.

2. Lösung nach Anspruch 1, wobei das Alkalimetallhydroxid Natrium- oder Kaliumhydroxid ist, das in einer Menge vorliegt, die ausreicht, um einen pH von 12 bis 14 zu erzeugen.

3. Lösung nach Anspruch 1, wobei das wasserlösliche Nickelsalz Nickelsulfamat ist, das in einer Menge von 0,01 Mol pro Liter bis 0,15 Mol pro Liter vorliegt.

4. Lösung nach Anspruch 1, wobei das chelatbildende Mittel Ethylendiamin ist und das molare Konzentrationsverhältnis von chelatbildendem Mittel zu Nickelsalz 4/1 bis 12/1 beträgt.

5. Lösung nach Anspruch 1, wobei der Ethylenethioharnstoff in einer Menge von $0,49 \times 10^{-5}$ bis $3,9 \times 10^{-5}$ Mol pro Liter vorliegt.

chemistry was maintained as follows: nickel cation (Ni^{+2}) 5600 ppm to 6400 ppm (0.095 to 0.109 mole per liter nickel sulfamate tetrahydrate); ethylenediamine, 47000 to 53000 ppm (0.782 to 0.883 mole per liter); borohydride anion (BH_4^{-1}) 125 to 177 ppm (8.46 to 11.90, $\times 10^{-3}$ mole per liter sodium borohydride); ethylenethiourea, 1.1 to 1.6 ppm (1.08 to 1.57, $\times 10^{-6}$ mole per liter).

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The plating bath is ideally operated utilizing an automated analysis/solution replenishment system. Such a system would incorporate a computer controlled solution replenishment feedback system with the high performance liquid and ion chromatography.

In addition to the improved luster resulting from the present process, higher density and improved wear resistance are also produced in the coated articles according to the present invention. It is also significant to note that the composition is thallium free. The elimination of the thallium in the solution produces a significant reduction in toxicity hazard for the platers. It should also be noted that being thallium free the plating solution is easier to handle in terms of hazardous waste and disposal.

Claims

1. A thallium free electroless nickel-boron plating solution comprising water, a water soluble nickel salt, a chelating agent, alkali metal hydroxide, a boron containing reducing agent and 0.098×10^{-5} mole per litre to 9.8×10^{-5} mole per litre of ethylenethiourea.

2. The solution of claim 1 wherein the alkali metal hydroxide is sodium or potassium hydroxide present in an amount sufficient to produce a pH of 12 to 14.

3. The solution of claim 1 wherein the water soluble nickel salt is nickel sulfamate present in an amount of 0.01 mole per liter to 0.15 mole per liter.

4. The solution of claim 1 wherein the chelating agent is ethylenediamine and the molar concentration ratio of chelating agent to nickel salt is 4/1 to 12/1.

5. The solution of claim 1 wherein the ethylenethiourea is present in an amount of 0.49×10^{-5} to 3.9×10^{-5} mole per liter.

6. The solution of claim 1 wherein the boron containing reducing agent is sodium borohydride present in an amount of 0.002 mole per liter to 0.052 mole per

liter.

7. A process of electroless plating a thallium free nickel-boron, coating onto a substrate material which comprises immersing the substrate in an aqueous solution comprising water, a water soluble nickel salt, a chelating agent, an alkali metal hydroxide, a boron containing reducing agent and 0.098×10^{-5} mole per litre to 9.8×10^{-5} mole per litre of ethylenethiourea, said solution being heated to a temperature of 85°C to 102°C (185°F to 215°F), and removing the substrate from the solution, resulting in a nickel boron coated substrate having improved wear resistance.

8. The process of claim 7 including maintaining concentrations of the solution components and the solution temperature constant throughout the plating process.

9. The process of claim 7 wherein the alkali metal hydroxide is sodium or potassium hydroxide present in an amount sufficient to produce a pH of 12 to 14.

10. The process of claim 7 wherein the water soluble nickel salt is nickel sulfamate present in an amount of 0.01 mole per liter to 0.15 mole per liter.

11. The process of claim 7 wherein the chelating agent is ethylenediamine and the molar concentration ratio of chelating agent to nickel salt is 4/1 to 12/1.

12. The process of claim 7 wherein the ethylenethiourea is present in an amount of 0.49×10^{-5} to 3.9×10^{-5} mole per liter.

13. The process of claim 7 wherein the substrate comprises titanium, steel, nickel, copper, aluminum or magnesium.

14. The process of claim 7 wherein the coating is at least $2.54 \mu\text{m}$ (0.1 mil) thick.

Patentansprüche

1. Thalliumfreie Lösung zum stromlosen Nickel-Bor-Auftragen, die aus Wasser, einem wasserlöslichen Nickelsalz, einem chelatbildenden Mittel, einem Alkalimetallhydroxid, einem Bor enthaltenden Reduktionsmittel und $0,098 \times 10^{-5}$ Mol pro Liter bis $9,8 \times 10^{-5}$ Mol pro Liter Ethylenthioharnstoff besteht.

2. Lösung nach Anspruch 1, wobei das Alkalimetallhydroxid Natrium- oder Kaliumhydroxid ist, das in einer Menge vorliegt, die ausreicht, um einen pH von 12 bis 14 zu erzeugen.

3. Lösung nach Anspruch 1, wobei das wasserlösliche Nickelsalz Nickelsulfamat ist, das in einer Menge von 0,01 Mol pro Liter bis 0,15 Mol pro Liter vorliegt.

4. Lösung nach Anspruch 1, wobei das chelatbildende Mittel Ethylendiamin ist und das molare Konzentrationsverhältnis von chelatbildendem Mittel zu Nickelsalz 4/1 bis 12/1 beträgt.

5. Lösung nach Anspruch 1, wobei der Ethylenthioharnstoff in einer Menge von $0,49 \times 10^{-5}$ bis $3,9 \times 10^{-5}$ Mol pro Liter vorliegt.



6. Lösung nach Anspruch 1, wobei das Bor enthaltende Reduktionsmittel Natriumborhydrid ist, das in einer Menge von 0,002 Mol pro Liter bis 0,052 Mol pro Liter vorliegt.

7. Verfahren zum stromlosen Auftragen eines thalliumfreien Nickel-Bor-Überzugs auf ein Substratmaterial durch Eintauchen des Substrats in eine wässrige Lösung aus Wasser, einem wasserlöslichen Nickelsalz, einem chelatbildenden Mittel, einem Alkalimetallhydroxid, einem Bor enthaltenden Reduktionsmittel und $0,098 \times 10^{-5}$ Mol pro Liter bis $9,8 \times 10^{-5}$ Mol pro Liter Ethylenthioharnstoff, wobei die Lösung auf eine Temperatur von 85°C bis 102°C (185°F bis 215°F) erhitzt wird, und Entnehmen des Substrats aus der Lösung, was einen mit Nickel und Bor überzogenes Substrat ergibt, das eine verbesserte Verschleißfestigkeit hat.

8. Verfahren nach Anspruch 7, beinhaltend das Konstanthalten der Konzentrationen der Lösungskomponenten und der Lösungstemperatur während des gesamten Auftragsverfahrens.

9. Verfahren nach Anspruch 7, wobei das Alkalimetallhydroxid Natrium- oder Kaliumhydroxid ist, das in einer Menge vorliegt, die ausreicht, um einen pH von 12 bis 14 zu erzeugen.

10. Verfahren nach Anspruch 7, wobei das wasserlösliche Nickelsalz Nickelsulfamat ist, das in einer Menge von 0,01 Mol pro Liter bis 0,15 Mol pro Liter vorliegt.

11. Verfahren nach Anspruch 7, wobei das chelatbildende Mittel Ethylendiamin ist und das molare Konzentrationsverhältnis von chelatbildendem Mittel zu Nickelsalz 4/1 bis 12/1 beträgt.

12. Verfahren nach Anspruch 7, wobei der Ethylenthioharnstoff in einer Menge von $0,49 \times 10^{-5}$ bis $3,9 \times 10^{-5}$ Mol pro Liter vorliegt.

13. Verfahren nach Anspruch 7, wobei das Substrat Titan, Stahl, Nickel, Kupfer, Aluminium oder Magnesium umfaßt.

14. Verfahren nach Anspruch 7, wobei der Überzug wenigstens 2,54 µm (0.1 mil) dick ist.

Revendications

1. Solution exempte de thallium pour la métallisation autocatalytique au nickel-bore, comprenant de l'eau, un sel de nickel hydrosoluble, un agent de chélation, un hydroxyde de métal alcalin, un agent réducteur contenant du bore et de $0,098 \times 10^{-5}$ mole par litre à $9,8 \times 10^{-5}$ mole par litre d'éthylenthio-urée.

2. Solution selon la revendication 1, dans laquelle l'hydroxyde de métal alcalin est l'hydroxyde de sodium ou de potassium présent en une quantité suffisante pour obtenir un pH de 12 à 14.

3. Solution selon la revendication 1, dans laquelle le sel de nickel hydrosoluble est le sulfamate de nickel présent en une quantité de 0,01 mole par litre à 0,15

mole par litre.

4. Solution selon la revendication 1, dans laquelle l'agent de chélation est l'éthylènediamine et le rapport quant à la concentration molaire entre l'agent de chélation et le sel de nickel est de 4/1 à 12/1.

5. Solution selon la revendication 1, dans laquelle l'éthylène-thio-urée est présente en une quantité de $0,49 \times 10^{-5}$ à $3,9 \times 10^{-5}$ mole par litre.

6. Solution selon la revendication 1, dans laquelle l'agent de réduction contenant du bore est le borohydrure de sodium présent en une quantité de 0,002 mole par litre à 0,052 mole par litre.

7. Procédé de déposition autocatalytique d'un revêtement au nickel-bore exempt de thallium, sur une matière de substrat, qui consiste à plonger le substrat dans une solution aqueuse comprenant de l'eau, un sel de nickel hydrosoluble, un agent de chélation, un hydroxyde de métal alcalin, un agent réducteur contenant du bore et de $0,098 \times 10^{-5}$ mole par litre à $9,8 \times 10^{-5}$ mole par litre d'éthylène-thio-urée, ladite solution étant chauffée à une température de 85°C à 102°C (185°F à 215°F), et à retirer le substrat de la solution, ce qui donne lieu à un substrat enduit de nickel-bore manifestant une résistance améliorée à l'usure.

8. Procédé selon la revendication 7, englobant le fait de maintenir constantes les concentrations des composants de la solution, ainsi que la température de la solution tout au long du processus de métallisation.

9. Procédé selon la revendication 7, dans lequel l'hydroxyde de métal alcalin est l'hydroxyde de sodium ou de potassium présent en une quantité suffisante pour obtenir un pH de 12 à 14.

10. Procédé selon la revendication 7, dans lequel le sel de nickel hydrosoluble est le sulfamate de nickel présent en une quantité de 0,01 mole par litre à 0,15 mole par litre.

11. Procédé selon la revendication 7, dans lequel l'agent de chélation est l'éthylènediamine et le rapport quant à la concentration molaire entre l'agent de chélation et le sel de nickel est de 4/1 à 12/1.

12. Procédé selon la revendication 7, dans lequel l'éthylène-thio-urée est présente en une quantité de $0,49 \times 10^{-5}$ à $3,9 \times 10^{-5}$ mole par litre.

13. Procédé selon la revendication 7, dans lequel le substrat comprend du titane, de l'acier, du nickel, du cuivre, de l'aluminium ou du magnésium.

14. Procédé selon la revendication 7, dans lequel le revêtement a une épaisseur d'au moins 2,54 µm (0.1 millième de pouce).

