

[54] **ARTICLES AND METHOD OF
ELECTRODEPOSITING A
DECORATIVE NICKEL/CHROMIUM
COATING ON A METAL SUBSTRATE**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 80,725, Oct. 14, 1970, abandoned.

[30] **Foreign Application Priority Data**

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[51] **Int. Cl.****C23b 5/50**

[58] **Field of Search**204/41, 49, 43 T,
204/16; 29/183.5, 194, 196.6, 196.3, 195

[56] **References Cited**

UNITED STATES PATENTS

346,258 7/1886 Bates.....204/49

2,844,530 7/1958 Wesley et al.204/49 X
3,268,424 8/1966 Brown et al.204/41
3,298,802 1/1967 Odekerken204/41 X
3,449,223 6/1969 Odekerken204/41
3,644,183 2/1972 Odekerken204/41 X

Primary Examiner—G. L. Kaplan

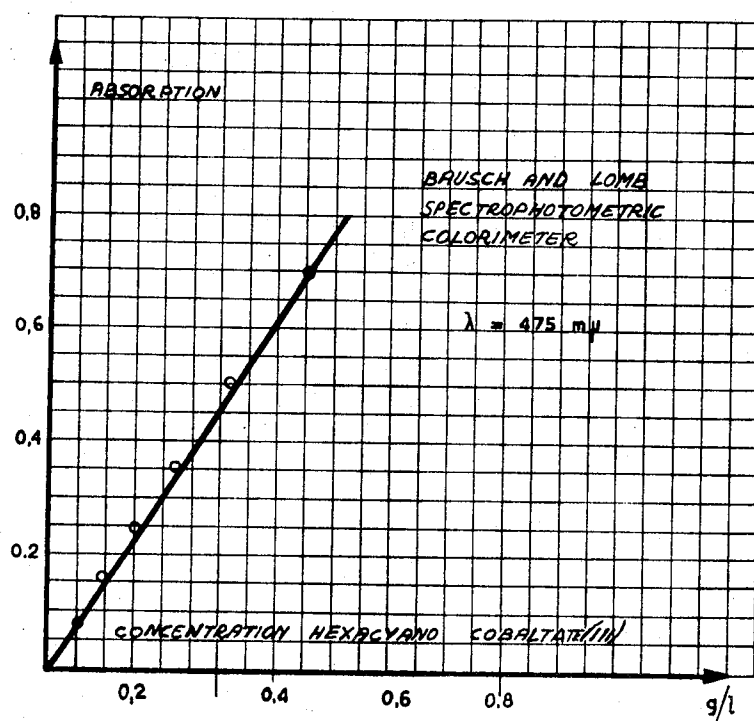
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[57]

ABSTRACT

A method of electrodepositing a decorative nickel/chromium coating on a metal substrate, which comprises, as its essential step, before a final chromium plating step, electroplating on the substrate a nickel layer containing fine particles of a solid, non-conductive material embedded therein. Improved results are achieved when the nickel layer is electroplated from an aqueous nickel-plating bath containing dispersed therein from 0.1 to 10.0 g/l of microcrystalline particles of a nickel compound, which is insoluble in the bath, selected from the group consisting of the compounds having the formula $Ni_x[M(CN)_yA_z]$ and compounds having the formula $Ni_x[M(SCN)_y]$ wherein M is a transition metal, A is NO_2^- or CO, z is 0 or 1, $y+z$ is the coordination number of the transition metal, and x is the number of nickel atoms saturating the valence of the complex portion of the nickel compound.

13 Claims, 1 Drawing Figure



ARTICLES AND METHOD OF ELECTRODEPOSITING A DECORATIVE NICKEL/CHROMIUM COATING ON A METAL SUBSTRATE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of applicant's copending application, Ser. No. 80,725 filed on Oct. 14, 1970, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an improved method of electrodepositing a decorative, corrosion-resistant nickel-chromium coating on a metal substrate. More specifically, this invention relates to improvements in a method of the aforesaid type, which comprises, as its featuring step, electroplating on the substrate a nickel layer which contains particles of a solid, non-conductive material embedded therein, which cause, in a subsequent chromium plating step, the deposition of a micro-porous chromium layer.

2. Description of the Prior Art

It has long been known that in order to improve the resistance to outdoor corrosion of a decorative nickel-chromium coating on a metal substrate, the chromium layer should be micro-cracked or micro-porous so as to leave the underlying nickel layer partially uncovered, and therefore a number of methods have been developed in order to achieve this purpose.

For instance, the so-called "duplex method" (AES Proceedings 47 (1960), 214-225) entails the deposition of a two-layer chromium system on a nickel layer. After deposition of a first crack-free, internally stressed chromium layer from a first plating bath, a second micro-cracked layer of chromium is deposited from a different plating bath, under operating conditions which cause the first chromium layer to become micro-cracked in a fine pattern.

This method presents several drawbacks. Firstly, it leads to an increased consumption of expensive chromic anhydride and to an increased length of time (by a factor of more than 5) for the electro-deposition. Moreover, the resulting microcracks are sparse, or even absent, in parts of the workpiece furthest away from the anode of the electrolytic cell, and consequently the finished workpiece has a non-uniform resistance to corrosion. Furthermore, deposition of chromium or chromium is far from being easily and satisfactorily achieved.

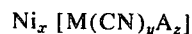
U.S. Pat. No. 3,298,802 to J.M. Odekerken overcomes such drawbacks, since it teaches to avoid the two-layer chromium system deposition. This patent discloses a method for obtaining a micro-porous deposit of chromium which comprises depositing, after a first layer of bright nickel and before the final chromium layer, an "intermediate" layer of nickel from a bath containing solid particles in the form of a fine dispersion of an inert material "as conductive as or less conductive than graphite". These particles are held in suspension in the bath by mechanical means (by stirring or injecting air into the bath) and become embedded in the layer of nickel which is being deposited; on account of the low conductivity of the particles, "no chromium layer can precipitate on the non- or ill conducting "places", as formed by the solid particles, so an

interruption in the chromium layer takes place. In this manner a microporous chromium layer will originate at once". The particles, whose size should be kept below 10 microns and preferably below 1 micron, "may be made up out of aluminum oxide, silicon carbide, chromous oxide, ceric oxide, diamond powder" or, alternatively, formed in the galvanic bath itself by adding BaCl_2 or H_2S to a solution of nickel sulphate, thus forming BaSO_4 or NiS_2 , or adding silver carbonate to nickel chloride thus forming silver chloride. Reference is also made to the use of positively charged metal hydroxide sols which are of colloidal size, as iron hydroxide, indium hydroxide, aluminum hydroxide and thorium hydroxide.

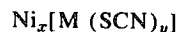
This method, though excellent in principle, possesses several major disadvantages which are strictly related to the nature of the solid particles dispersed in the nickel plating bath from which the intermediate layer is to be deposited. In fact, none of the foregoing materials has been found actually suitable to meet the stringent requirements of an industrial nickel electroplating bath. For instance, very large amounts of the aforesaid inert materials are needed, the optimum concentration ranging from 100 to 200 grams per liter, which result in the presence and progressive increase of muddy deposits in the bath with consequent blocking of the air-injection nozzles and, ultimately, shut-down of the electrolytic cell. Moreover, the life of a plating bath containing the foregoing materials is very short, since they show phenomena of hydration and hence of gelling with progressive lowering of the quality of the bath, which leads in the long run to impaired adhesion between the nickel and chromium layers and roughness of the surfaces of the workpieces with attendant loss of their brilliance. As a consequence, the electrolytic bath requires frequent renewal. It is therefore apparent that a burdensome increase of the operating and maintenance costs is caused by the use of the aforesaid inert materials in electroplating baths.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has now been found that improved results are achieved in a method of electrodepositing a decorative, corrosion resistant nickel-chromium coating on a metal substrate, by electroplating on the substrate a nickel layer from an aqueous nickel plating bath containing a dispersion of solid, non-conductive particles, and successively electroplating a chromium layer on the underlying nickel layer, provided that the solid, non-conductive particles consist of a nickel compound selected from the group consisting of the compounds having the formula



and compounds having the formula



wherein:

M is a transition metal;

A is NO_2^- or CO

z is 0 or 1

y + z is the coordination number of the transition metal, and

x is the number of nickel atoms saturating the valence of the complex portion of the aforesaid nickel compound.

Thus, it has been found that the present invention provides an improved method which overcomes all the above-mentioned drawbacks.

It has, in fact, been found that the particles of the foregoing nickel compounds are in the form of microcrystalline aggregates which do not show any phenomena of hydration and hence of gelling and, therefore, the life of the baths containing them is substantially unlimited. Besides, since a markedly lower amount of these nickel compounds as inert material is needed in order to obtain a microporous chromium over nickel coating having excellent corrosion resistance in comparison with the large quantities of solids used in the prior art method, there is no danger of muddy deposits in the bath with attendant risks both for the electrolytic cell operation and quality of the coated workpiece.

BRIEF DESCRIPTION OF THE DRAWING

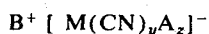
The FIGURE is a graphic illustration of a calibration curve of a Bausch and Lomb spectrometric colorimeter, showing the absorption of nickel-plating bath samples in relation to the concentration of a nickel compound in accordance with the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

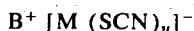
Among the compounds falling within the scope of the foregoing formulas, the following ones are particularly preferred: nickel nitropentacyanoferrate (II), nickel carbonilpentacyanoferrate (II), nickel hexacyanocobaltate (II), nickel tetracyanoplatinate (III), nickel tetrathiocyanatoplatinate (II), nickel hexacyanoferrate (II), nickel hexacyanoferrate (III), nickel hexacyanomanganate (II), nickel hexacyanomanganate (III), nickel coppercyanate (II), nickel coppercyanate (I), nickel hexacyanoiridate (III), nickel hexacyanoruthenate (II), nickel nitropentacyanoruthenate (III), nickel hexacyanorhodate (III), nickel tetracyanopalladate (II), nickel tetrathiocyanatopalladate (II), nickel hexathiocyanatoplatinate (IV), and nickel tetracyanonickelate (II).

The concentration of the foregoing nickel compounds in the nickel plating bath is preferably from 0.1 to 10.0 grams per liter.

Although the nickel compound can be prepared in a separate vessel and thereafter uniformly dispersed in the nickel-plating bath, in accordance with a preferred embodiment of the present invention a dispersion of microcrystalline aggregates of the nickel compound is formed in situ, within the electrolytic cell, by adding to the nickel plating bath a water-soluble salt selected from the group consisting of the compounds having the formula:



and the compounds having the formula:



wherein B is an alkali metal, and M, A, y and z are as above identified. The sodium and potassium salts are particularly suitable.

Measurement of the concentration of the added nickel compound is easily made at any time by taking off a small sample from the bath, cooling it to room temperature and measuring the absorption, e.g. in a Bausch and Lomb spectrophotometric colorimeter, at a wave length $\lambda = 475 \mu$ which corresponds to maxi-

mum absorption in a nickel bath. The absorption value is then correlated with the concentration using a calibration curve such as, for example, that shown in the drawing, in which the abscissa gives the concentration in grams per liter of hexacyanocobaltate (III) and the ordinate gives the measured value of the absorption.

Within the scope of the present invention, by "nickel-plating bath" any conventional Watts type nickel bath is meant. It is well known that a "Watts bath" is an aqueous solution of $NiSO_4 \cdot 7H_2O$ and $NiCl_2 \cdot 6H_2O$ buffered with boric acid, to which brighteners, wetting agents, etc. can be added. Concentrations of from about 200 to 300 grams per liter of $NiSO_4 \cdot 7H_2O$, 40 to 60 grams per liter of $NiCl_2 \cdot 6H_2O$ and 40 to 50 grams per liter of H_3BO_3 are generally used.

Among the metal substrates suitable for electroplating by the improved method of the present invention are iron, aluminum, zinc, copper, magnesium and their alloys.

Although the nickel layer containing embedded in it the microcrystalline particles in accordance with this method may be deposited directly on the metal workpiece to be coated, it is preferred to electroplate on the workpiece a base layer of copper or nickel. It should therefore be understood that by "metal substrate" is meant not only the metal workpiece to be coated but also any copper or nickel layer which may be suitably deposited as a base layer. Either a bright nickel layer or a dull nickel layer can be plated as base nickel layers.

The thickness of the particle-containing nickel layer should be sufficient to firmly anchor the particles. With a thickness of this layer of only 0.1 micron the positive effect of the nickel-containing layer is observable. In order to obtain the best results it is, however, advisable to have a thickness of 1 to 3 microns; any greater thickness does not improve the resistance to corrosion, and does not affect the glossiness of the deposit.

As taught by the above-mentioned U.S. Pat. No. 3,298,802, whose relevant disclosures are incorporated by reference in the present specification, the particles should be of as small size as possible, since the smaller their size the thinner the nickel layer including them. The average particle size preferably ranges between 0.5 and 5 microns. It has been found that the number of particles embedded in the nickel layer is on the average in excess of $10^6/cm^2$ and, accordingly, the number of pores in the chromium layer is also in excess of $10^6/cm^2$. The large number of pores, their extreme fineness and the uniformity of their distribution are the causes of the high resistance to corrosion of the metal substrates dealt with. The number of pores per unit of surface area is only slightly influenced by the current density and hence by the shape of the workpiece.

The operating conditions under which electrodeposition of the copper or nickel base layer, if any, takes place as well as deposition of the particle-containing layer and final microporous chromium layer are those conventionally used in the electrochemical art and, therefore, will be readily apparent to anyone having ordinary skill in this art. It is also apparent that the electroplating conditions can be varied within somewhat wide limits, depending for instance on the layer thickness, which, for the particle-containing nickel layer, will in turn depend on the average particle size. For instance, a current density of about 4-5 amperes/cm² in

the nickel-plating step and about 18÷20 amperes/cm² in the chromium plating step will be generally used.

The following examples will further illustrate the invention.

Example 1

An object made of "Zamak" (an aluminum-zinc alloy), coated with a layer of copper having a thickness of 30 microns, was nickel plated for 2 minutes in a bright nickel plating bath kept in agitation by blowing air into it, under the following conditions:

current density — 4A/dm²

temperature — 60°C

pH — 4.5

The bath contained:

Nickel sulphate, NiSO₄·7H₂O — 250 grams per liter

Nickel chloride, NiCl₂·6H₂O — 50 grams per liter

Boric acid, H₃BO₃ — 50 grams per liter

o-benzoyl sulphonimide — 6 grams per liter

2-butyne-1,4-diol — 150 milligrams per liter

Nickel hexacyanocobaltate obtained by adding to the foregoing 0.2 grams per liter of potassium hexacyanocobaltate (III). Hexacyanocobaltate (III) ions reacted with the Ni²⁺ ions, thus forming a fine dispersion of insoluble, microcrystalline particles of nickel hexacyanocobaltate (III) having average particle size ranging from about 1 to about 5 microns.

Electrodeposition of a nickel layer having particles of nickel hexacyanocobaltate (III) embedded in it took place. The thickness of this layer was 2 microns. The nickel-plated object was then chromium-plated for 2 minutes, at a current density of 20 A/dm², at 40°C, in a conventional chromium plating bath containing 300 grams per liter of CrO₃ and 2.5 grams per liter of H₂SO₄. The chromium layer thus obtained had a thickness of 0.25 microns and a number of pores of about 10⁶/cm².

Example 2

An object made of "Zamak" alloy, coated with a layer of copper having a thickness of 30 microns, was nickel-plated to a thickness of 19 microns in a conventional Watts type nickel bath. The nickel-plated object was then immersed, without intermediate rinsing, in a bright nickel plating bath having the same composition as that given in Example 1. In this bath the object was electroplated for a period of one minute at 60°C at a current density of 4A/dm². An electrodeposited nickel layer containing particles of nickel hexacyanocobaltate (III) embedded in it was obtained. The thickness of this layer was about 0.8 micron.

The nickel-plated object was then chromium-plated in a conventional chromium-plating bath, having the same composition as that shown in Example 1, under the same operational conditions.

The resistance to corrosion of the object thus electroplated was found to be markedly improved as compared with an object which had undergone a treatment identical to the previous one except that no nickel hexacyanocobaltate (III) was contained in the nickel-plating bath.

Example 3

An iron object covered with a layer of copper of a thickness of 8 microns, was electroplated with a layer of nickel of a thickness of 15 microns in a conventional Watts type nickel plating bath; without intermediate

rinsing, the object was then immersed in a second bath which contained:

nickel sulphate, NiSO₄·7H₂O — 300 grams per liter

nickel chloride, NiCl₂·6H₂O — 60 grams per liter

Boric acid, H₃BO₃ — 40 grams per liter

sodium naphthalentrisulphonate — 6 grams per liter

2-butyne-1,4-diol — 180 milligrams per liter

nickel tetracyanoplatinate obtained by adding to the foregoing 0.3 grams per liter of potassium tetracyanoplatinate (II).

The object was electroplated for 2 minutes under the following conditions:

current density — 4A/dm²

temperature — 60°C

pH — 4.5

Electrodeposition of a nickel layer having particles of nickel tetracyanoplatinate (II) embedded in it took place. The thickness of this layer was 1 micron. After a conventional chromium plating step carried out under the same operational conditions as shown in Example 1, the resulting resistance to corrosion, compared with that of an object which had undergone a treatment identical to the previous one, except that no nickel tetracyanoplatinate (II) was contained in the nickel-plating bath, was clearly enhanced.

Example 4

An object of ferrous material, after a conventional pickling and degreasing step, was treated for 16 minutes in a conventional semi-bright nickel bath of the "sulphur-free" type. Then, it was immersed without intermediate rinsing in a nickel-plating bath which contained:

nickel sulphate, NiSO₄·7H₂O — 300 grams per liter

nickel chloride, NiCl₂·6H₂O — 60 grams per liter

boric acid, H₃BO₃ — 40 grams per liter

sodium alkylpyridinesulphonate — 1 gram per liter

sodium naphthalenetrisulphonate — 6 grams per liter
nickel hexacyanoferrate (II) obtained by adding to the foregoing 0.3 grams per liter of potassium hexacyanoferrate (II).

After electroplating for 3 minutes at a current density of 3A/dm² and a temperature of 55°C, a 7-micron thick layer having particles of nickel hexacyanoferrate (II) embedded in it, was obtained. After a conventional chromium-plating step carried out under the same operational conditions as shown in Example 1, the resistance of the object to corrosion was clearly superior to that of an object which had undergone a treatment identical to the previous one, except that no nickel hexacyanoferrate (II) was contained in the nickel-plating bath.

Example 5

An object of ferrous material after coating with a 15-micron thick layer of copper and a 20-micron layer of nickel, was immersed without intermediate rinsing in a bright nickel-plating bath which contained:

nickel sulphate, NiSO₄·7H₂O — 300 grams per liter

nickel chloride, NiCl₂·6H₂O — 60 grams per liter

boric acid, H₃BO₃ — 50 grams per liter

2-butyne-1,4-diol — 120 milligrams per liter

sodium naphthalenetrisulphonate — 2 grams per liter

sodium metabenzenedisulphonate — 4 grams per liter

nickel hexacyanoferrate (III) obtained by adding to the foregoing 0.4 grams per liter of potassium hexacyanoferrate (III).

After electroplating for 2 minutes, under the following conditions:

temperature — 55°C

current density — 4A/dm²

pH — 4.5

a 3-micron thick nickel layer having particles of nickel hexacyanoferrate (III) embedded in it was obtained.

After a conventional chromium plating step carried out under the same operational conditions as shown in Example 1, the resistance to corrosion of the object was clearly superior to that of an object which had undergone a treatment identical to the previous one, except that no nickel hexacyanoferrate (III) was contained in the nickel-plating bath.

Example 6

Two series of identical iron sheets (50 cm × 30 cm × 3 mm), coated with a copper layer having thickness of 30 microns, were separately nickel-plated at a current density of 5A/dm², at a temperature of 60°C, by successively electroplating for 1 minute the first series sheets in a same nickel bath having composition as shown in Example 1, and the second series sheets in a bath having composition identical to the previous one, except that, instead of nickel hexacyanocobaltate (III), 100 grams per liter of silica having average particle size of 0.2 micron were used, as shown in Example 1 of the above-mentioned U.S. Pat. No. 3,298,802.

The baths were periodically replenished so as to keep their compositions substantially constant throughout the whole run. The nickel-plated sheets of both series were then subjected to the same chromium-plating step in a conventional bath having the composition shown in Example 1.

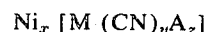
After nickel-plating of the 6th sheet, the silica-containing bath began to show gelling phenomena which increased rapidly until, after nickel-plating of the 9th sheet, the presence of muddy deposit in the bath caused obstruction of the air-injection nozzles and the run ought to be therefore discontinued. The decreasing quality of the bath resulted in attendant progressively poor outdoor properties of the nickel/chromium plated sheets. The seventh sheet in the series and the following ones showed very poor adhesion between the adjacent chromium and nickel layers, as was proved by bending the sheets on a sharp edge which resulted in delamination of the surface which moreover was rough and dull.

On the contrary, when the first series run was discontinued after having electroplated 20 sheets, the insoluble nickel compound-containing bath showed no deterioration phenomena of any kind, and the iron sheet which was nickel/chromium plated last showed the same valuable properties, especially in regard to protection against outdoor corrosion, adhesion between adjacent layers, surface smoothness and gloss, as the sheet which was plated first.

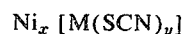
What is claimed is:

1. In a method of electrodepositing a decorative, corrosion resistant coating on a metal substrate, said coating comprising a microporous chromium layer on a nickel layer having embedded therein particles of a solid, non-conductive material, by electroplating on the substrate said nickel layer from an aqueous nickel plat-

ing bath containing suspended therein a dispersion of said solid, non-conductive particles; and thereafter electroplating a chromium layer on said nickel layer from an aqueous chromium plating bath, the improvement wherein said solid, non-conductive particles consist of a nickel compound selected from the group consisting of the compounds having the formula



and compounds having the formula



wherein:

M is a transition metal;

A is NO₂⁻ or CO

z is 0 or 1

y + z is the coordination number of the transition metal, and

x is the number of nickel atoms saturating the valence of the complex portion of the aforesaid nickel compound.

2. The method of claim 1, wherein said metal substrate is a metal layer on a metal workpiece.

3. The method of claim 2, wherein said metal layer is a copper layer.

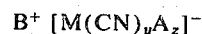
4. The method of claim 2, wherein said metal layer is a bright nickel layer.

5. The method of claim 2, wherein said metal layer is a dull nickel layer.

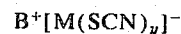
6. The method of claim 1, wherein said nickel compound is selected from the group consisting of nickel nitropentacyanoferrate (II), nickel carbonilpentacyanoferrate (II), nickel hexacyanocobaltate (II), nickel tetracyanoplatinate (III), nickel tetrathio-cyanatoplatinate (II), nickel hexacyanoferrate (II), nickel hexacyanoferrate (III), nickel hexacyanomanganate (II), nickel hexacyanomanganate (III), nickel coppercyanate (II), nickel coppercyanate (I), nickel hexacyanoiridate (III), nickel hexacyanoauruthenate (II), nickel nitro-pentacyanoauruthenate (III), nickel hexacyanorhodate (III), nickel tetracyanopalladate (II), nickel tetrathiocyanatopalladate (II), nickel hexathio-cyanatoplatinate (IV) and nickel tetracyanonickelate (II).

7. The method of claim 1, wherein the concentration of the nickel compound in the nickel plating bath is from 0.1 to 10.0 grams per liter.

8. The method of claim 1, wherein the nickel compound is formed in situ by adding to the nickel plating bath a water-soluble salt selected from the group consisting of the compounds having the formula



and the compounds having the formula



wherein

B is an alkali metal,

M is a transition metal,

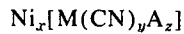
A is NO₂⁻ or CO

z is 0 or 1 and

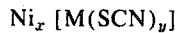
y + z is the coordination number of the transition metal

9. An article comprising a decorative, corrosion resistant nickel/chromium coating on a metal substrate comprising as its essential layer a nickel layer having embedded therein microcrystalline, non-conductive

particles of a nickel compound, said nickel compound being selected from the group consisting of the compounds having the formula:



and compounds having the formula:



wherein:

M is a transition metal;

A is NO_2^- or CO

z is 0 or 1

y + z is the coordination number of the transition metal, and x is the number of nickel atoms saturating the valence of the complex portion of the afore-

10. The article of claim 9, wherein said nickel compound is selected from the group consisting of nickel nitropentacyanoferrate (II), nickel carbonilpentacyanoferrate (II), nickel hexacyanocobaltate (II), 20

nickel tetracyanoplatinate (III), nickel tetrathiocyanatoplatinate (II), nickel hexacyanoferrate (II), nickel hexacyanoferrate (III), nickel hexacyanomanganate (II), nickel hexacyanomanganate (III), nickel coppercyanate (II), nickel coppercyanate (I), nickel hexacyanoiridate (III), nickel hexacyanoruthenate (II), nickel nitro-pentacyanoruthenate (III), nickel hexacyanorhodate (III), nickel tetracyanopalladate (II), nickel tetrathiocyanatopalladate (II), nickel hexathiocyanatoplatinate (IV) and nickel tetracyanonickelate (II).

11. The article of claim 10, wherein said chromium layer is a microporous chromium layer on said nickel layer.

12. The article of claim 10, wherein the thickness of said nickel layer is from about 1 to about 3 microns.

13. The article of claim 12, wherein the average particle size of said microcrystalline non-conductive particles is from about 0.5 micron to about 5.0 microns.

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