United States Patent Office 3,528,894
Patented Sept. 15, 1970

3,528,894

METHOD OF ELECTRODEPOSITING CORROSION RESISTANT COATING

William B. Stoddard, Jr., Matawan, and Warren H. McMullen, East Brunswick, N.J., assignors to M & T Chemicals Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed Aug. 25, 1966, Ser. No. 574,923
Int. Cl. C23b 5/08, 5/46, 5/50
U.S. Cl. 204—40 13 Claims

ABSTRACT OF THE DISCLOSURE

In accordance with certain of its aspects, this invention relates to novel products and to a process for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance which comprises electrodepositing onto a basis metal first nickel plate having a low tensile stress of less than about 2100 kg./cm.^{2}; and electrodepositing into said first nickel plate an outer nickel plate having a high tensile stress of at least about 8400 kg./cm.^{2} and a thickness of about 0.1–0.5 micron.

This invention relates to a novel electroplating process. More particularly, it relates to a novel process for electroplating a nickel deposit characterized by its protective action and its ability to be chromium plated to yield a product which is highly resistant to corrosion.

As is well known to those skilled in the art, a chromium plated product may be prepared by depositing on a basis metal a first plate of semi-bright nickel characterized by its ductility and leveling; a second plate of bright nickel; and a final chromium plate. Although this system may permit attainment of a product characterized by improved resistance to corrosion, it has been found not to be satisfactory under extreme conditions. For example, if such a system be subjected to three cycles of the standard CASS Test (ASTM designation B380–61T), it will be found that the surface will show definite evidence of corrosion resulting in loss of surface brilliance and attractiveness. These effects are regarded as indicating unsatisfactory performance over the extended course of the three cycles of the test. For many uses, it is desired to prepare a chromium plated article characterized by its ability to resist atmospheric corrosion after extended periods of time equivalent to three cycles of these tests.

It is an object of this invention to provide a novel nickel plate characterized by its ability to receive a chromium plate having improved resistance to corrosion. It is another object of this invention to provide a novel chromium plate characterized by its high resistance to corrosion, particularly under conditions of extended duration. Other objects will be apparent to those skilled in the art from inspection of the following description.

In accordance with certain of its aspects, the novel process of this invention for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance comprises electrodepositing onto a basis metal first nickel plate having a low tensile stress of less than about 2100 kg./cm.^{2}; and electrodepositing onto said first nickel plate an outer nickel plate having a high tensile stress of at least about 8400 kg./cm.^{2} and a thickness of about 0.1–0.5 micron.

The basis metal which may be plated in accordance with the process of this invention may be iron including iron alloys such as steel; copper; nickel; brass; bronze; zinc; or alloys of any of these metals; etc. The outstanding results of this invention may be particularly apparent when the basis metal is steel. It is a particular feature of

the novel process of this invention that it may permit attainment of plated products having outstanding and unexpected properties when the material on which the plate may be deposited is a zinc-base die casting.

In accordance with certain of its aspects, the first step of the process of this invention may include deposition onto the basis metal of deposit of copper hereinafter referred to as the "base copper plate." In the case of zinc-base die castings, this may be essential; in the case of other basis metals, e.g. steel, it may be omitted. Deposition onto the zinc-base die casting of the desired base copper plate may be effected by depositing copper for example from a cyanide-copper plating bath. Typically such a bath may have the composition set forth in Table I wherein all values are in grams per liter (g./l.) except where otherwise indicated:

TABLE I

Component	Minimum	Maximum	Preferred
Cu [1]	45	60	52
Free KCN (or NaCN)	15	22	18

[1] Added as copper cyanide CuCN.

Deposition of the base copper plate may be carried out by electroplating for 8–12 minutes, say 10 minutes at 60° C.–70° C., say 65° C., and cathode current density of 3–6 a.s.d., say 4.5 a.s.d. Preferably the bath may be agitated as by air agitation or cathode rocker. During this time copper may be deposited having a thickness of 7.5–15 microns, typically 12 microns.

The basis metal, typically either (a) a zinz-base die casting bearing the hereinbefore disclosed base copper plate or (b) a steel basis metal which may optionally bear a base copper plate, may then be further treated in accordance with the process of this invention. Preferably there may be deposited upon the basis metal, including the zinc-base die casting bearing the base copper plate, a first layer of a sulfur-free, ductile, semi-bright nickel plate. The semi-bright nickel plate may typically be deposited by electro-deposition from a Watts-type bath, a fluoborate-type bath, a chloride-free sulfate bath, a sulfamate bath, a chloride-free sulfamate bath, etc. or by other means including decomposition of nickel carbonyl with resultant deposition of nickel.

A typical Watts bath which may be used in practice of this invention may include the following components in aqueous solution, all values being in grams per liter (g./l.) except for the pH (nickel chloride used may be $NiCl_2 \cdot 6H_2O$; nickel sulfate may be $NiSO_4 \cdot 6H_2O$. When nickel chloride or sulfate is referred to in the tables, the hexahydrate is intended.):

TABLE II

Component	Minimum	Maximum	Preferred
Nickel sulfate·$6H_2O$	200	500	300
Nickel chloride·$6H_2O$	30	80	45
Boric acid	35	55	45
Semi-bright additive	0.2	3	0.75
pH electrometric	3	5	4.0

A typical sulfamate-type bath which may be used in the practice of this invention may include the following components:

TABLE III

Component	Minimum	Maximum	Preferred
Nickel sulfamate	330	600	375
Nickel chloride·$6H_2O$	15	60	45
Boric acid	35	55	45
Semi-bright additive	0	3	0.75
pH electrometric	3	5	4.0

A typical fluoborate-type bath which may be used in the practice of the invention may include the following components:

TABLE IV

Component	Minimum	Maximum	Preferred
Nickel fluorate	250	400	300
Nickel chloride·$6H_2O$	10	60	20
Boric acid	15	30	20
Semi-bright additive	0.2	3	0.75
pH electrometric	2	4	3.0

A typical chloride-free sulfate-type bath which may be used in practice of this invention may include the following components:

TABLE V

Component	Minimum	Maximum	Preferred
Nickel sulfate·$6H_2O$	300	500	400
Boric acid	35	55	45
Semi-bright additive	0.2	3	0.75
pH electrometric	3	5	4.0

A typical chloride-free sulfamate-type bath which may be used in practice of this invention may include the following components:

TABLE VI

Component	Minimum	Maximum	Preferred
Nickel sulfamate	300	600	350
Boric acid	35	55	45
Semi-bright additive	0.2	3	0.75
pH electrometric	3	5	4.0

It will be apparent that the above baths may contain components in amounts falling outside the preferred minima and maxima set forth; but most satisfactory and economical operation may normally be effected when the components are present in the baths in the amounts indicated.

Semi-bright additives which may be employed in practice of this first step of the process of this invention (using the baths of Tables II–VI) may typically include, for example, coumarin, butyne diol, chloral hydrate, formaldehyde, piperonal, diethoxylated butyne diol, bromal hydrate, etc. The preferred semi-bright additive may be coumarin used in concentration of 0.2–3 g./l. typically 0.75 g./l.

Electrodeposition of the first, sulfur-free, ductile semi-bright nickel plate may be carried out from the semi-bright plating baths of Tables II–VI, by use of a cathode current density of 1–10 a.s.d., say 5 a.s.d., at temperature of 50–60° C., say 55° C. for 20–30 minutes, typically 25 minutes. During this time, it may be possible to deposit on the basis metal a deposit of semi-bright nickel typically having a thickness of 5–40 microns, say 25 microns.

The semi-bright nickel plate may be essentially sulfur-free, i.e. contain less than about 0.004% sulfur and typically 0.002%–0.004%, and sometimes as low as 0.0010%–0.0015% sulfur. The ductility of the semi-bright plate may be such that $T/2R$ may have a value of about 0.5 when measured by the well-known standard Chrysler Micrometer Test.

It will be found that the first nickel plate deposited in accordance with practice of this invention may have a low tensile stress of less than about 2100 kg./cm.^{2}. Typically, the tensile stress of this first nickel plate may be measured by standard procedures using the Brenner-Senderhoff Contractometer which permits reading of tensile stress directly. Typically, the tensile stress of the first nickel plate may be 700–2100 kg./cm.^{2}; commonly it may be 1400 kg./cm.^{2} (kilograms per square centimeter).

In accordance with practice of the preferred embodiment of this invention, there may be electrodeposited onto the first nickel plate having a low tensile stress of less than about 2100 kg./cm.^{2}, a layer of bright nickel plate. The results of this invention may be achieved by the use of either the first semi-bright layer without presence of this layer of bright nickel plate or by use of the second layer of bright nickel plate without the first or semi-bright layer. It may be found however that outstanding and unexpected results, in terms of extended corrosion life, may be achieved when both the first semi-bright layer and the second layer of bright nickel plate are present.

Electrodeposition of bright nickel may be carried out by plating from baths containing nickel sulfate; a chloride, typically nickel chloride; a buffering agent, typically boric acid; and a wetting agent. Such baths may include the Watts bath and the high chloride bath. Other baths may contain, as the source of the nickel, a combination of nickel fluoborate with nickel sulfate and nickel chloride, or a combination of nickel sulfamate and nickel chloride. Typical Watts-type baths and high chloride baths are noted in Tables VII and VIII.

TABLE VII.—WATTS-TYPE BATHS

Components	Minimum	Maximum	Preferred
Nickel sulfate·$6H_2O$	200	400	300
Nickel chloride·$6H_2O$	30	75	60
Boric acid	30	50	40
Temperature, (° C.)	38	65	50
Agitation	Mechanical and/or air or solution plumbing		
pH	2.5	4.5	3.5

TABLE VIII.—HIGH CHLORIDE BATHS

Components	Minimum	Maximum	Preferred
Nickel chloride·$6H_2O$	150	300	225
Nickel sulfate·$6H_2O$	40	150	85
Boric acid	30	50	40
Temperature (° C.)	38	65	55
Agitation	Mechanical and/or air or solution pumping		
pH	2.5	4.5	3.5

There may also be present in the electroplating bath of Tables VII–VIII primary nickel brighteners in amount of 0.002–0.2 g./l., say 0.2 g./l.; secondary brighteners in amount of 1–300 g./l., say 5 g./l. and secondary auxiliary brighteners in amount of 0.5–3 g./l., say 1 g./l. Typical primary brighteners may include acetylenic compounds such as butyne diol, diethoxylated butyne diol, phenyl propiolamide or pyridinium compounds such as quaternized prridine derivatives e.g., α,α' bis (pyridinium iodide)2,6-lutidine. Typical secondary brighteners may include e.g. sulfo-oxygen compounds typified by saccharin benzene monosulfonate etc. Typical secondary auxiliary brighteners may include sodium allyl sulfonate, sodium 3-chloro butene 1-sulfonate.

Deposition of the bright nickel plate may be carried out at temperatures of 40–60° C., say 50° C. at pH of 2.5–4.5, say 3.5 for 8–14 minutes, say 10 minutes to permit attainment of a bright nickel plate having a thickness of 7–12 microns, say 10 microns. This bright nickel plate may commonly be found to have a low tensile stress which is typically compressive e.g. +700 to minus 700 kg./cm.^{2} and commonly zero to minus 700 kg./cm.^{2}. A minus designation indicates a compressive stress.

In practice of the novel process of this invention, there may be deposited into the first nickel plate having a low tensile stress (optionally but preferably bearing a layer of a second or bright nickel plate), an outer nickel plate having a tensile stress at least about 8400 kg./cm.^{2} and a thickness of 0.1–0.5 microns.

Deposition of high tensile stress outer nickel plate may be carried out preferably by immersing the basis metal bearing said plates(s) into an electroplating bath containing (a) nickel ion, (b) nickel chloride $NiCl_2 \cdot 6H_2O$, (c) nickel fluoborate $Ni(BF_4)_2$, (d) a primary brightener, (e) a secondary brightener, (f) an additive heterocyclic having at least two nitrogen atoms in an otherwise carbocyclic ring structure. Typically such baths may be as noted in Table IX.

TABLE IX

Components	Minimum	Maximum	Preferred
Ni^{++}	120	187	150
Nickel chloride·$6H_2O$	110	225	150
Nickel fluoborate	300	900	450
Primary brightener	0.002	0.4	0.2
Secondary brightener	0.1	1	0.25
Additive	0.1	0.8	0.25
Temperature (° C.)	20	65	55
Agitation	Mechanical and/or air or solution pumping		
pH	3	5	4

The primary brighteners which may be used in this step of this invention may include those materials (present in very low or relatively low concentrations, typically 0.002-0.4 g./l., say 0.2) which by themselves may or may not produce any visible brightening action.

These primary brighteners may permit attainment of bright nickel deposits when used in combination with secondary brighteners. Secondary brighteners, which are ordinarily used in combination with primary brighteners but in higher concentrations, typically 0.1 g./l–1 g./l., may produce some brightening or grain refining effect, but when used alone do not have mirror bright deposits at desired brightening rates. Typical primary brighteners which may be used in this step of the process of this invention may include acetylenic compounds such as butyne diol, diethoxylated butyne diol, phenyl propiolamide, propargyl alcohol, 3-butyne 1-ol, 2-methyl-3-butyne-2-ol or pyridinium compounds such as quaternized pyridine derivaitves. Typical secondary brighteners which may be used in this step of the process of this invention may include e.g. sulfo-oxygen compounds such as saccharin, sodium benzene monosulfonate, sodium vinyl sulfonate, sodium metabenzene disulfonate, etc.

The preferred primary brightener may be acetylenic compounds, typicaly 2-butyne diol-1,4 and the preferred secondary brighteners may be sulfo-oxygen containing compounds, preferably saccharin.

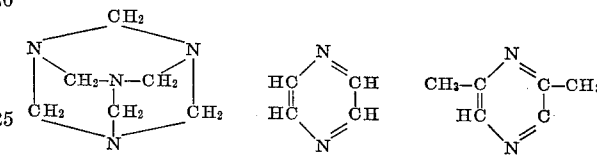
The electroplating baths from which the high tensile stress outer nickel plate may be deposited may contain an additive heterocyclic chemical compound having at least two nitrogen atoms in an otherwise carbocyclic ring structure. These heterocyclic compounds may be monocyclis, dicyclic, bicyclic, tricycli, etc. although commonly they may be monocyclic. They may contain 2,3,4, etc. nitrogen atoms in an otherwise carbocyclic ring structure. Typical ring structures which may be employed may include: pyrazole (i.e 1,2-diazole), 2-isoimidazole (i.e. 1,3-isodiazole), 1,2,3-triazole, 1,24-triazole, pyridazine (i.e. 1,2-diazine), pyrimidine (i.'e.' 1,3-diazine), pyrazine (i.e. 1,4-diazine), piperazine, s-triazine (i.e. 1,3,5-triazine), astriazine (i.e. 1,2,4-triazine), v-triazine (i.e. 1,2,3-triazine), 1,5-pyrindine (i.e. 4-pyrindine), isoindazole (i.e. benzpyrazole), cinnoline (i.e. 1,2-benzodiazine), quinazoline (i.e. 1,3-benzodiazine), naphthyridine, pyrido [3,4-b]-pyridine, pyrido [3,2-b]-pyridine,pyrido [4,3-b]-pyridine, purine, hexamethylenetetramine, bis-pyridinum compounds.

Inertly substituent compounds having the above ring structures may be employed. Typical inert substituents which may be borne by any of these rings may include inert hydrocarbon groups, typified by aromatic groups such as naphthyl, xylene, tolyl, or aliphatic groups typified by alkyl groups, methyl, ethyl, propyl, and butyl. The preferred substituents may include lower alkyl, e.g. those having less than 5–6 carbon atoms; and these lower alkyl groups may be substituted on the carbon atoms present, on the nitrogen atoms present (e.g. 2,6-dimethyl pyrazine) or they may be present as bridging groups forming additional rings (as may be the case with 1:1' ethylene, 2:2' dipyridinium halides such as the dibromide or the dichloride). The additive heterocyclic compounds may have one or more of their nitrogen atoms quaternized as by reaction of the heterocyclic compound with hydrochloric acid, hydrobromic acid, sulfuric acid, etc.; in this latter instance, compounds otherwise of lesser utility because of their low solubility may be rendered substantially more soluble in quarternized form.

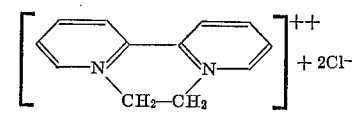
Typical illustrative compounds which may be employed in practice of this invention may be the following: s-triazine, u-triazine, v-triazine, pyridazine, pyrimidine, indole, isobenzazole, pyrindine, isoindazole, cinnoline, quinazoline, naphthyridine, pyrido[3,4-b]pyridine, pyrido [3,2-b]pyridine, pyrido[4,3-b]pyridine, hexamethylene tetramine, piperazine, pyrazine, 2,6-dimethyl pyrazine.

Although it may be found that substantially improved results may be achieved in practice of the instant invention by using additive heterocyclic compounds falling within the above categories, outstandingly superior results may be achieved by use of the following specific illustrative compounds:

(I) hexamethylene tetramine
(II) pyrazine
(III) 2,6-dimethyl pyrazine
(IV) 1:1' ethylene 2:2' dipyridinium dichloride



(I) (II) (III)



(IV)

These additive heterocyclic compounds may be present in the baths to produce the high tensile stress outer nickel plate in effective amounts which may typically be 0.1–0.8 g./l., typically about 0.25 g./l. Preferably the compound employed may be used in the form of its quaternized compound (i.e. at least one of the nitrogen atoms may be quaternized) with e.g. hydrochloric acid or a hydrocarbon halide such as methyl chloride.

The preferred additive heterocyclic compound may be 1:1' ethylene 2:2' dipyridinium dichloride, typically available under the trademark "Ortho di Quat" sold by the California Chemical Company.

Typical illustrative baths which may be used in this step of the process of this invention may contain the following:

TABLE X

Components	Minimum	Maximum	Preferred
Ni^{++}	120	187	150
Nickel chloride·$6H_2O$	110	225	150
Nickel fluoborate	300	900	450
Primary brightener e.g. butyne diol	0.002	0.4	0.2
Secondary brightener e.g. saccharin	0.1	1	0.25
Additive e.g. 1:1'ethylene 2:2'dipyridinium dichloride	0.1	0.8	0.25

TABLE XI

Components	Minimum	Maximum	Preferred
Ni^{++}	120	187	150
Nickel chloride·$6H_2O$	110	225	150
Nickel fluoborate	300	900	450
Primary brightener e.g. butyne diol	0.002	0.4	0.2
Secondary brightener e.g. sacchairn	0.1	1	0.25
Additive compound e.g. hexamethylene tetramine	0.1	0.8	0.25

TABLE XII

Components	Minimum	Maximum	Preferred
Ni^{++}	120	187	150
Nickel chloride·$6H_2O$	110	225	150
Nickel fluoborate	300	900	450
Primary brightener e.g. butyne diol	0.002	0.4	0.2
Secondary brightener e.g. saccharin	0.1	1	0.25
Additive compound e.g. pyrazine	0.1	0.8	0.25

Deposition of the high stress nickel deposit or plate may be carried out at 40° C.–60° C., say 50° C. at pH of 2.5–4.5, say 3.5, for 0.5–2 minutes, say 1 minute to permit attainment of a bright nickel plate having a thickness of 0.1–0.5 micron, say 0.25 micron.

It is a particular feature of the so-deposited outer nickel plate that it has a high tensile stress of at least about 8400 kilograms per square centimeter as measured by the Brenner-Senderhoff Contractometer. Normally the high tensile strength of this novel deposit may be 8400–14,000 kg./cm.^{2} and typically it may be 9800 kg./cm.^{2}. It is a feature of this outer nickel plate that it may be mirror bright and when deposited in the manner hereinbefore set forth, may permit attainment of a highly leveled mirror bright surface particularly characterized by its ability to receive a chromium plate and which will permit attainment of a chromium plated composite having an unexpected degree of resistance to corrosion.

Chromium may be deposited on the bright nickel plate in accordance with the practice of the process of this invention by deposition from the chromium plate bath having the composition set forth in Table XIII.

TABLE XIII

Component	Minimum	Maximum	Preferred
CrO_3	250	400	250
$SO_4^=$	2.5	4.0	2.5

Sulfate may be provided in the form of sodium sulfate or sulfuric acid. There may also be present in the chromium plating bath other ingredients typified by those which render the bath self-regulating or high speed. Typical of such other components in the bath may be strontium ion (provided in the form of strontium sulfate or strontium chloride) or $SiF_6^=$ provided in the form of potassium silicofluoride.

Chromium plating in accordance with the process of this invention may be carried out at 45° C.–55° C., say 50° C. for 2–4 minutes, say 3 minutes with a cathode current density of 12–20 a.s.d., say 14 a.s.d. Typically this may permit attainment of a chromium plate having a thickness of 0.1–1.0 micron, say 0.25 micron.

It is a particularly outstanding feature of the novel product of this invention that it is extremely resistant to the effects of corrosive atmosphere over an extended period of time. It may be found, for example, that if a chromium plated product, prepared in accordance with the process of this invention, be subjected to severe corrosive conditions as, for example, in the CASS Test or Corrodkote Test, this novel product may unexpectedly exhibit substatnially no visible corrosion at the end of three cycles of the test. Typical bright chromium plated deposits may, even under the most favorable conditions, exhibit a substantially noticeable degree of corrosion after the first cycle of the Corrodkote Test.

Practice of the novel process of the invention may be observed from the following illustrative examples wherein, unless otherwise indicated, all parts are parts by weight.

EXAMPLES

In these examples unless otherwise specifically indicated, plating was carried out on a 1010 alloy steel basis metal plate having a thickness of about 1.5 mm. and dimensions of 10 cm. x 15 cm.

In all cases, unless otherwise specified, the steel was given a normal cleaning cycle prior to further treating to remove rust spots, grease, oil, etc. No copper plate was applied to the steel before further treating.

Where a semi-bright nickel plate was deposited onto the clean steel basis metal, it was deposited from a nickel plating bath containing 45 g./l. of nickel chloride·$6H_2O$, 300 g./l. of nickel sulfate·$6H_2O$, 45 g./l. of boric acid and 0.75 g./l. of coumarin with the electrometric pH maintained at about 4.0. Plating was carried out at cathode current density of 5 a.s.d. at 55° C. for 25 minutes to yield a deposit of semi-bright nickel having a thickness of 25 microns.

Where a bright nickel deposit is referred to in these examples, this was obtained by electrodeposition from a plating bath containing 60 g./l. of nickel chloride·$6H_2O$, 300 g./l. of nickel sulfate·$6H_2O$, 40 g./l. of boric acid, and butyne diol as a primary brightener in amount of 0.2 g./l., saccharin as a secondary brightener in amount of 1 g./l., and butyne diol monosulphonate as a secondary auxiliary brightener in amount of 1 g./l. The bath was maintained at electrometric pH of 3.5 during the 10 minutes of electroplating at 50° C. to permit attainment of a bright nickel plate having a thickness of 10 microns.

Electrodeposition of the highly tensile stressed nickel plate in practice of this invention was carried out in these examples from a bath containing 150 g./l. nickel chloride·$6H_2O$, 450 g./l. nickel fluoroborate, 0.2 g./l. of butyne diol primary brightener, 0.25 g./l. of saccharin secondary brightener together with designated amounts, as hereinafter indicated, of additive heterocyclic compound. The bath was maintained at an electrometric pH of 4 and a temperature of 55° C. during the plating time which varied as hereinafter set forth to produce the thickness of plate.

Where decorative chromium plate is referred to, it was obtained by deposition from a bath containing 250 g./l. chromic acid and 25 g./l. of sulfate provided as sulfuric acid. Deposition for three minutes at cathode current density of 14 a.s.d. permitted attainment of a decorative chromium plate having a thickness of 0.25 micron. Here, as elsewhere, the abbreviation "a.s.d." designates amperes per square decimeter.

Example 1

In this control example, the standard steel basis metal panel was plated with semi-bright nickel plate, bright nickel plate, and then chromium plate.

Example 2

In this example, which represents practice of a preferred embodiment of the process of this invention, the standard steel basis metal panel was plated with semi-bright nickel plate, bright nickel plate, and high tensile stress nickel. The high tensile stress nickel was plated from a bath containing 0.25 g./l. of hexamethylenetetramine for 1 minute to yield a plate 0.5 micron thick.

Example 3

In this example, which represents practice of a preferred embodiment of the process of this invention, the standard steel basis metal panel was plated with semi-bright nickel plate, bright nickel plate, and high tensile stress nickel. The high tensile stress nickel was plated from a bath containing 0.25 g./l. of pyrazine for 1 minute to yield a plate 0.5 micron thick.

Example 4

In this example, which represents practice of a preferred embodiment of the process of this invention, the standard steel basis metal panel was plated with semi-bright nickel plate, bright nickel plate, and high tensile stress nickel. The high tensile stress nickel was plated from a bath containing 0.25 g./l. of 2,6-dimethylpyrazine for 1 minute to yield a plate 0.5 micron thick.

Example 5

In this example, which represents practice of a preferred embodiment of the process of this invention, the standard steel basis metal panel was plated with semi-bright nickel plate, bright nickel plate, and high tensile stress nickel. The high tensile stress nickel was plated from a bath containing 0.25 g./l. of piperazine for 1 minute to yield a plate 0.5 micron thick.

Example 6

In this example, which represents practice of a preferred embodiment of the process of this invention, the standard steel basis metal panel was plated with semi-bright nickel plate, bright nickel plate, and high tensile stress nickel. The high tensile stress nickel was plated from a bath containing 0.25 g./l. of 1:1′ ethylene, 2:2′ dipyridinium-dichloride for 1 minute to yield a plate 0.5 micron thick.

Example 7

In this control example, the standard steel basis metal panel was plated with a bright nickel plate and then chromium plated.

Example 8

In this control example, the standard steel basis metal panel was plated with a semi-bright nickel plate and then chromium plated.

Example 9

In this example, which represents practice of a preferred embodiment of the process of this invention, the standard steel basis metal panel was plated with bright nickel plate, a plate of high tensile stress nickel, for 1 minute in a bath containing 0.25 g./l. of hexamethylenetetramine (to obtain a high tensile stress nickel plate of 0.5 micron thickness) and then chromium plated.

Example 10

In this example, which represents practice of a preferred embodiment of the process of this invention, the standard steel basis metal panel was plated with semi-bright nickel plate, a plate of high tensile stress nickel, for 1 minute in a bath containing 0.25 g./l. of hexamethylenetetramine (to obtain a high tensile stress nickel plate of 0.5 micron thickness), and then chromium plated.

Example 11

In this example, which illustrates practice of the process of this invention, the standard zinc base die casting having a thickness of 1.5 cm. and dimensions 10 cm. x 10 cm. was first plated with copper from a bath containing 52 g./l. of copper (added as copper cyanide) and 18 g./l. of sodium cyanide. Electroplating was carried out at 65° C. for 10 minutes with cathode rocker agitation at a cathode current density of 4.5 a.s.d. to yield a copper plate having a thickness of 12 microns. The die casting was then given a plate of semi-bright nickel, a bright nickel plate, and high tensile stress nickel plate, and a chromium plate.

Example 12

In this control example, the standard zinc base die casting was treated exactly as in Example 11 except that the high tensile stress nickel plate was not electrodeposited.

Each of the 12 steel basis metal panels or zinc base die casting panels of these examples was subjected to the standard CASS Test hereinbefore detailed. The test was carried out by maintaining each panel under test conditions for three 16 hour cycles and after the test the surface was examined for visible corrosion which was recorded as heavy, light or none.

TABLE XIV

Example:	Remarks
1 (control)	Heavy
2	None
3	None
4	None
5	None
6	None
7 (control)	Heavy
8 (control)	Heavy
9	Light
10	Light
11	None
12 (control)	Heavy

Inspection of the samples at the end of the three cycles of the CASS Test indicated that the control samples of Examples 1, 7, 8, and 12 were heavily corroded, all of the other specimens showed substantially no corrosion, but were mirror bright in appearance. Panels of Examples 9 and 10 indicated a high resistance to corrosion under the test conditions and showed only a minimum number of surface imperfections and no gross rust spots or indications of severe perforation of the nickel surface. The panels of Examples 2–6, and 11 showed a highly outstanding resistance to corrosion; in fact at the conclusion of the very severe test they were substantially identical in brightness to examples before the test.

Comparison of Example 1 (which is typical of prior art chromium plated duplex nickel) with Examples 2–6, (which are illustrative of the process of this invention) clearly demonstrates the superiority of the novel process of this invention. Similarly comparison of control Examples 7–8 with experimental Examples 9–10 clearly demonstrates the superiority of the novel process; and comparison of control Example 12 with experimental Example 11 particularly shows the outsanding results attained in the case of zinc base die castings.

Thus from Table XIV it will be apparent that the novel process of this invention permits attainment of a chromium plate product which is characterized by its unexpectedly high resistance to corrosion. It will be particularly apparent that the panels prepared in accordance with the preferred embodiments of the process of this invention (Examples 2–6 and 11) are particularly outstanding.

It is a particularly unexpected feature of this invention that the novel outer nickel plate is characterized by an unexpectedly high tensile stress of at least about 8400 kg. per cm.^{2} at the preferred thickness of 0.1–0.5 micron.

Although this invention has been disclosed by reference to preferred illustrative examples, it will be apparent to those skilled in the art that various modifications and changes may be made thereto which fall within the scope of this invention.

What is claimed is:

1. The process for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance which comprises electrodepositing onto a basis metal a first nickel plate having a low tensile stress of less than about 2100 kg./cm.^{2}; and electrodepositing onto said first nickel plate an outer nickel plate having a high tensile stress of at least about 8400 kg./cm.^{2} and a thickness of about 0.1–0.5 micron wherein said outer nickel plate is deposited from an aqueous electroplating bath containing an effective amount of an additive heterocyclic compound, said amount being sufficient to increase the tensile stress of said outer nickel plate to at least 8400 kg./cm.^{2} as compared to a lower tensile stress without said additive heterocyclic compound and wherein said heterocyclic compound is selected from the group consisting of hexamethylene tetramine, piperazine, pyrazine, 2,6-dimethyl pyrazine, and 1:1′ ethylene 2:2′ dipyridinium dichloride.

2. The process as claimed in claim **1** for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance wherein said outer nickel plate is deposited from a bath containing as additive heterocyclic compound 1:1′ ethylene 2:2′ dipyridinium dichloride.

3. The process as claimed in claim **1** for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance wherein said first nickel plate is a sulfur-free semi-bright nickel plate.

4. The process as claimed in claim **1** for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion re-

sistance wherein said first nickel plate is a bright nickel plate.

5. The process as claimed in claim 1 for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance wherein said nickel plate includes a layer of sulfur-free semi-bright nickel plate under a layer of bright nickel plate.

6. The process for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance which comprises electrodepositing onto a basis metal a first nickel plate having a low tensile stress of less than about 2100 kg./cm.^{2}; immersing said first nickel plate as cathode into an aqueous electroplating bath containing 120 g./l.–187 g./l. Ni^{++}, 110 g./l.–225 g./l. $NiCl_2 \cdot 6H_2O$, 150 g./l.–450 g./l. $Ni(BF_4)_2$, primary brightener, secondary brightener, and an effective amount of an additive heterocyclic compound, said amount being sufficient to increase the tensile stress of said outer nickel plate to at least 8400 kg./cm.^{2} as compared to a lower tensile stress without said additive heterocyclic compound and wherein said heterocyclic compound has at least two nitrogen atoms in an otherwise carbocyclic ring structure; maintaining an anode in said bath; passing current between said anode and said cathode thereby depositing on said cathode an outer nickel plate having a tensile stress of at least about 8400 kg./cm.^{2} and a thickness of about 0.1–0.5 micron.

7. The process as claimed in claim 6 for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance wherein said additive heterocyclic compound is present in amount of 0.1 g./l.–0.8 g./l.

8. The process as claimed in claim 7 for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance wherein said additive heterocyclic compound is selected from the group consisting of hexamethylene tetramine, piperazine, pyrazine, 2,6-dimethyl pyrazine, and 1:1′ ethylene 2:1′ dipyridinium dichloride.

9. The process as claimed in claim 8 for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance wherein said additive heterocyclic compound is 1:1′ ethylene 2:2′ dipyridinium dichloride.

10. The process for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance which comprises electrodepositing onto a basis metal a first nickel plate having a low tensile stress of less than about 2100 kg./cm.^{2}; and immersing said first nickel plate as cathode into an aqueous electroplating bath containing 120 g./l.–187 g./l. Ni^{++}, 110 g./l.–225 g./l. $NiCl_2 \cdot 6H_2O$, 150 g./l.–450 g./l. $Ni(BF_4)_2$, primary brightener, secondary brightener, and 0.1 g./l.–0.8 g./l. of an additive selected from the group consisting of hexamethylene tetramine, piperazine, pyrazine, and 2,6-dimethyl pyrazine; maintaining an anode in said bath; passing current between said anode and cathode thereby depositing on said cathode an outer nickel plate having a tensile stress of at least about 8400 kg./cm.^{2} and a thickness of about 0.1–0.5 micron.

11. An electroplating bath for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance comprising in aqueous solution

	G./l.
Ni^{++}	120–187
$NiCl_2 \cdot 6H_2O$	110–225
$Ni(BF_4)_2$	150–450

together with primary brightener, secondary brightener, and an effective amount of additive heterocyclic compound said amount being sufficient to increase the tensile stress of said outer nickel plate to at least 8400 kg./cm.^{2} as compared to a lower tensile stress without said additive heterocyclic compound and wherein said heterocyclic compound has at least two nitrogen atoms in an otherwise carbocyclic ring structure.

12. An electroplating bath as claimed in claim 11 comprising in aqueous solution

	G./l.
Ni^{++}	120–187
$NiCl_2 \cdot 6H_2O$	110–225
$Ni(BF_4)_2$	150–450

together with primary brightener, secondary brightener, and an effective amount of additive heterocyclic compound said amount being sufficient to increase the tensile stress of said outer nickel plate to at least 8400 kg./cm.^{2} as compared to a lower tensile stress without said additive heterocyclic compound and wherein said heterocyclic compound is selected from the group consisting of hexamethylenetetramine, piperazine, pyrazine, 2,6-dimethyl pyrazine and 1:1′ ethylene 2:2 dipyridinium dichloride.

13. An electroplating bath as claimed in claim 12 comprising in aqueous solution

	G./l.
Ni^{++}	120–187
$NiCl_2 \cdot 6H_2O$	110–225
$Ni(BF_4)_2$	150–450

together with primary brightener, secondary brightener, and 0.1–0.8 g./l. of said heterocyclic compound.

References Cited

UNITED STATES PATENTS

2,326,999	8/1943	Lind et al.	204—49
2,513,280	7/1950	Brown	204—49
2,523,161	9/1950	Struyk et al.	204—49
2,839,459	6/1958	Foulke et al.	204—49
2,879,211	3/1959	Kardos et al.	204—40 XR
3,183,067	5/1965	Du Rose et al.	204—40 XR
3,388,049	6/1968	De Castelet	204—41 XR

FOREIGN PATENTS

789,887	1/1958	Great Britain.

GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.

29—183.5, 194, 196.6; 204—41, 49