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3,474,010

METHOD OF ELECTROPLATING CORROSION
RESISTANT COATING

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ABSTRACT OF THE DISCLOSURE

A process of coating an article with a corrosion res-
istant electroplate which comprises a first nickel plate
and a subsequent microcracked nickel plate thereon
capable of receiving a chromium plate. The microcracked
nickel plate is electrodeposited from an aqueous bath com-
prising 120–187 g./l. Ni⁺⁺, 110–125 g./l. NiCl₂·6H₂O
and 300–900 g./l. Ni(BF₄)₂ and which may additionally
contain brightener additives.

This invention relates to a novel electroplating process.
More particularly, it relates to a novel process for elec-
troplating a nickel deposit characterized by its protec-
tive 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 chromi-
um plated product may be prepared by depositing on
a basis metal a first plate of semi-bright nickel charac-
terized 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 ex-
ample, 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 evi-
dence of corrosion resulting in loss of surface brilliance
and attractiveness. These effects are regarded as indi-
cating 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 charac-
terized 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 a first sulfur-con-
taining bright nickel plate; immersing said first sulfur-
containing bright nickel plate into an aqueous electro-
plating bath containing about 120–187 g./l. Ni⁺⁺, 110–
225 g./l. NiCl₂·6H₂O, and 300–900 g./l. Ni(BF₄)₂, and
electrodepositing at least 0.6 micron of an outer micro-
cracked nickel plate from said bath.

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 outstand-
ing results of this invention may be particularly ap-
parent when the basis metal is steel. It is a particular
feature of the novel process of this invention that it may

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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 progress of this invention may include depo-
sition onto the basis metal of a deposit of copper here-
inafter 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

	Minimum	Maximum	Preferred
Component:			
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 zinc-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 de-
posited by electrodeposition from a Watts-type bath, a
sulfamate bath, a fluoborate-type bath, a chloride-free
sulfate 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
NiCl₂·6H₂O; nickel sulfate may be NiSO₄·6H₂O. When
nickel chloride or sulfate is referred to in the tables, the
hexahydrate is intended):

TABLE II

	Minimum	Maximum	Preferred
Component:			
Nickel sulfate-6H ₂ O.....	200	500	300
Nickel chloride-6H ₂ O.....	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 com-
ponents:

TABLE III

	Minimum	Maximum	Preferred
Component:			
Nickel sulfamate.....	330	600	375
Nickel chloride-6H ₂ O.....	15	60	45
Boric acid.....	35	55	45
Semi-bright additive.....	0	3	0.75
pH electrometric.....	3	5	4.0

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

TABLE IV

	Minimum	Maximum	Preferred
Component:			
Nickel fluoborate.....	250	400	300
Nickel chloride-6H ₂ O.....	10	60	20
Boric acid.....	15	30	20
Semi-bright additive.....	0.2	3	0.75
pH electrometric.....	2	4	3.0

It will be obvious to those skilled-in-the-art that one may use (here or elsewhere) either pure nickel fluoborate or commercial nickel fluoborate containing boric acid which may stabilize the fluoborate ion.

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

TABLE V

	Minimum	Maximum	Preferred
Component:			
Nickel sulfate-6H ₂ O.....	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

	Minimum	Maximum	Preferred
Component:			
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.

In accordance with practice of the preferred embodiment of this invention, there may be electrodeposited a layer of bright nickel plate onto the first nickel plate. The results of this invention may be achieved by the use of the second layer of bright nickel plate with or 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.

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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

	Minimum	Maximum	Preferred
Components:			
Nickel sulfate-6H ₂ O.....	200	400	300
Nickel chloride-6H ₂ O.....	30	75	40
Boric acid.....	30	50	40
Temperature, ° C.....	38	65	50
Agitation.....	(1)	(1)	(1)
pH.....	2.5	4.5	3.5

¹ Mechanical and/or air or solution pumping, etc.

TABLE VIII.—HIGH CHLORIDE BATHS

	Minimum	Maximum	Preferred
Components:			
Nickel chloride-6H ₂ O.....	150	300	225
Nickel sulfate-6H ₂ O.....	40	150	35
Boric acid.....	30	50	40
Temperature, ° C.....	38	65	55
Agitation.....	(1)	(1)	(1)
pH.....	2.5	4.5	3.5

¹ Mechanical and/or air or solution pumping.

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 1-30 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 pyridine 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.

In practice of the novel process of this invention, there may be deposited onto the first nickel plate (optionally but preferably bearing a layer of a second or bright nickel plate), an outer micro-cracked nickel plate having a thickness of at least about 0.6 micron and typically 0.6-3 microns, preferably about 2 microns.

Deposition of the outer nickel plate may be carried out preferably by immersing the basis metal bearing said plate(s) into an electroplating bath containing (a) 120-187 g./l. nickel ion Ni⁺⁺, (b) 110-225 g./l. nickel chloride NiCl₂·6H₂O, (c) 300-900 g./l. nickel fluoborate Ni(BF₄)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

	Minimum	Maximum	Preferred
Components:			
Ni ⁺⁺	120	187	150
Nickel chloride-6H ₂ O.....	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.....	(1)	(1)	(1)
pH.....	3	5	4

¹ Mechanical and/or air or solution pumping.

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 compounds of 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 derivatives. 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, typically 2-butyne diol-1,4 and the preferred secondary brighteners may be sulfo-oxygen containing compounds, preferably saccharin.

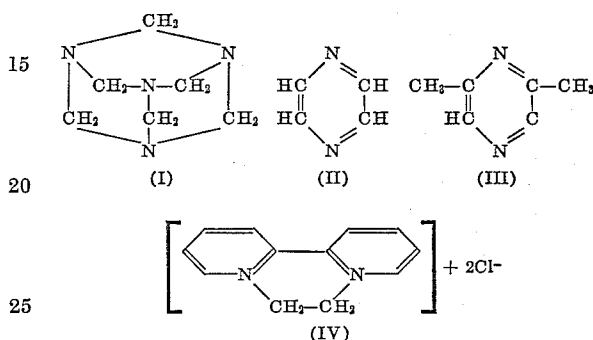
The electroplating baths from which the micro-crack outer nickel plate may be deposited may contain an additive heterocyclic chemical compound having at least two nitrogen atoms in an otherwise carbocyclic ring structure. These heterocyclic compounds may be monocyclic, bicyclic, tricyclic, etc. although 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-isimidazole (i.e. 1,3-isodiazole), 1,2,3-triazole, 1,2,4-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), as-triazine (i.e. 1,2,4-triazine), v-triazine (i.e. 1,2,3-triazine), 1,5-pyridine (i.e. 4-pyridine), 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-pyridinium compounds, etc.

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 quaternized 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, pyridine, 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, etc.

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



These additive heterocyclic compounds may be present in the baths to produce the micro-crack outer nickel plate in effective amounts to 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."

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 ₂ O.....	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 ₂ O.....	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. hexamethylene tetramine.....	0.1	0.8	0.25

TABLE XII

Components	Minimum	Maximum	Preferred
Ni ⁺⁺	120	187	150
Nickel chloride · 6H ₂ O.....	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 micro-cracked 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 2.4 minutes, say 2 minutes to permit attainment of a bright nickel plate having a thickness of at least about 0.6 micron, preferably 0.6–3 microns, say 1 micron.

It is a particular feature of the so-deposited nickel plate that it is characterized by its micro-cracked structure. Typically, when deposited in thicknesses of at least about 0.6 micron, and preferably 0.6–3 microns, say 1 micron, it is found that the deposit may contain at least about 10 cracks per cm., preferably about 100–600 cracks per cm., and typically about 250 cracks per cm. This micro-crack pattern at the noted thicknesses permits attainment of a bright to mirror-bright nickel plate which is characterized by its high resistance to corrosion as such.

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

Components	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 SiF₆⁼ 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 Corrodokote Test, this novel product may unexpectedly exhibit substantially 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 Corrodokote 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

6H₂O, 300 g./l. of nickel sulfate·6H₂O, 45 g./l. of boric acid, and 0.2 g./l. of 1,4-butyne diol with the electro-metric pH maintained at about 3.5. Plating was carried out at cathode current density of 6 a.s.d. at 55° C. for 35 minutes to yield a deposit of semi-bright nickel having a thickness of 30 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·6H₂O, 300 g./l. of nickel sulfate·6H₂O, 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 55° C. to permit attainment of a bright nickel plate having a thickness of 7.5 microns.

Electrodeposition of the micro-cracked nickel plate in practice of this invention was carried out in these examples from a bath containing 150 g./l. nickel chloride·6H₂O, 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 1.25 minutes at cathode current density of 21.6 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 bright nickel plate, and then chromium plated.

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 bright nickel plate, micro-crack nickel, for 2 minutes in a bath containing 0.25 g./l. hexamethylenetetramine, and then chromium plated.

Example 3

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

Example 4

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

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, micro-crack nickel, for 2 minutes in a bath containing 0.25 g./l. of hexamethylenetetramine and then chromium plated.

Example 6

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

Example 7

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, micro-crack nickel, and chromium. The micro-crack nickel was plated from a bath containing 0.25 g./l. of 1:1'ethylene, 2:2'dipyridinium-dichloride for 2 minutes to yield a plate 1.0 micron thick.

Each of the steel basis metal 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 as noted in Table XIII and after the test the surface was examined for basis metal corrosion. In Examples 6 and 7, the test used was the Corrodokote Test.

TABLE XIV

	Duration	Remarks
Example:		
1 (control).....	22 hours.....	100 rust spots.
2.....	107 hours.....	None.
3 (control).....	22 hours.....	50 rust spots.
4 (control).....	do.....	2 rust spots.
5.....	264 hours.....	None.
6 (control).....	60 hours.....	100 rust spots.
7.....	do.....	4 rust spots.

Inspection of the samples at the end of the three cycles of the test indicated that the control samples of Examples 1, 3, 4 and 6 were heavily corroded, all of the other specimens showed substantially no corrosion. Panels of Examples 2, 5, and 7 indicated a high resistance to corrosion under the test conditions and showed a minimum number of surface imperfections. The panel of Example 5 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.

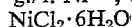
Comparison of Example 4 (which is typical of prior art chromium plated duplex nickel) with Examples 2, 5, and 7 (which are illustrative of the process of this invention) clearly demonstrates the superiority of the novel process of this invention.

Thus from Table XIII 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 (Example 2) are particularly outstanding.

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.

We claim:

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; immersing said first nickel plate into an aqueous bath containing about 120-187 g./l. Ni^{++} , 110-125 g./l.



and 300-900 g./l. $\text{Ni}(\text{BF}_4)_2$; and electrodepositing at least 0.6 micron of an outer microcracked nickel plate from said bath.

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 said electroplating bath containing, as brightener, an effective amount of an additive heterocyclic compound having at least two nitrogen atoms in an otherwise carbocyclic ring structure.

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 outer nickel plate is deposited from said electroplating bath containing, as brightener, an effective amount of an additive heterocyclic compound selected from the group consisting of hexamethylene tetramine, piperazine, pyrazine, 2,6-dimethyl pyrazine, and 1:1'ethylene 2:2' dipyridinium dichloride.

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 resistance wherein said outer nickel plate is deposited from said electroplating bath containing, as brightener, an effective amount of an additive heterocyclic compound 1:1' ethylene 2:2' di-pyridinium dichloride.

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 first nickel plate is a sulfur-free semi-bright nickel plate.

6. 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 bright nickel plate.

7. 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 includes a layer of sulfur-free semi-bright nickel plate under a layer of bright nickel plate.

8. 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; immersing said first nickel plate as cathode into an aqueous electroplating bath containing 120-187 g./l. Ni^{++} , 110-225 g./l. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 300-900 g./l. $\text{Ni}(\text{BF}_4)_2$, primary brightener, secondary brightener, and, as brightener, an effective amount of an additive heterocyclic compound having 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 and depositing on said cathode an outer microcracked nickel plate having a thickness of at least about 0.6 micron.

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 present in amount of 0.1-0.8 g./l.

10. The process as claimed in claim 9 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 2:2' dipyridinium dichloride.

11. The process as claimed in claim 10 for preparing a nickel surface characterized by its ability to receive a chromium plate possessing a high degree of corrosion resistance wherein said heterocyclic compound is 1:1' ethylene 2:2' dipyridinium dichloride.

12. 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 sulfur-containing bright nickel plate; and immersing said first nickel plate as cathode into an aqueous electroplating bath containing 120-187 g./l. Ni^{++} , 110-225 g./l. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 300-900 g./l. $\text{Ni}(\text{BF}_4)_2$, primary brightener, secondary brightener, and 0.1-0.8 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 and depositing on

said cathode an outer microcracked nickel plate having a thickness of at least about 0.6 micron.

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