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3,591,350

NOVEL PLATING PROCESS

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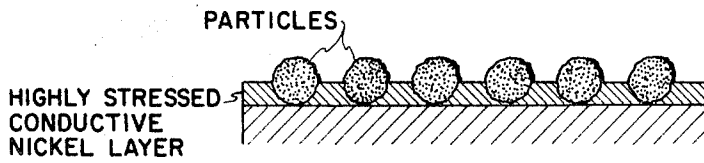


Figure 1

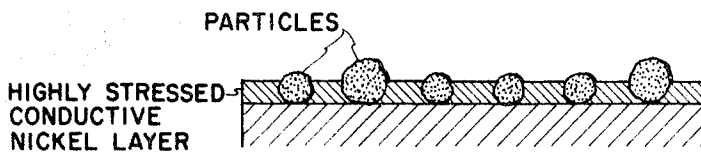


Figure 2

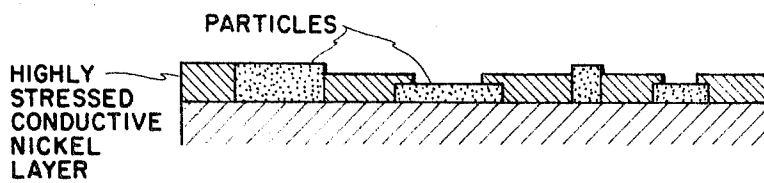


Figure 3

1

2

3,391,350

NOVEL PLATING PROCESS

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12 Claims

ABSTRACT OF THE DISCLOSURE

In accordance with certain of its aspects, the process of this invention for preparing a nickel plate receptive to a decorative chromium metal deposit, characterized by the presence of microporous areas and microcracked areas over substantially the entire surface of said chromium metal plate, comprises affixing to a basis material bearing a conductive metal surface a stratum of particles having a particle size of about 0.05–15 microns and a density on said conductive metal surface of about 100–5,000,000 particles/cm.²; and depositing in said stratum of particles a nickel layer having a high tensile stress of at least about 8,400 kg./cm.² and an effective thickness less than the maximum thickness of said stratum of particles thereby forming a matrix wherein said particles are retained affixed to said surface in fixed position in said nickel layer, and at least some of said particles intercept the surface of said nickel layer.

This invention relates to a novel process for preparing a metal plate particularly characterized by its receptivity to a metallic deposition, typified by a corrosion-resistant decorative electrodeposited chromium plate containing microcracked areas and microporous areas over substantially the entire surface of said chromium plate.

As is well known to those skilled-in-the-art, a decorative metallic deposition typified by chromium plate may be obtained by e.g. electrodepositing chromium onto a surface of electrodeposited nickel. However chromium plate obtained in this manner may be subject to defects including gross cracking or "crazing" and excessive corrosion which decreases usefulness as decorative chromium.

Prior art processes have attempted to overcome the problem of gross cracking in chromium plate by including in the nickel plating bath (from which may be deposited the nickel undercoat for the chromium plate) a substance which produces a microporous condition in the chromium plate subsequently deposited.

However prior art methods have not succeeded, by employing additives in the nickel plating bath, in preventing gross cracking over all areas of the subsequently deposited chromium plate and thus it has not been possible to attain a chromium plate characterized by the presence of microcracked areas and microporous areas over substantially the entire surface of said chromium plate.

It is an object of this invention to permit attainment of a plate particularly characterized by its receptivity to a metallic deposition typically a decorative chromium plate. It is a further object of this invention to provide a chromium plate which is highly useful as a decorative chromium plate, and which contains microcracked areas and microporous areas over substantially the entire surface area of said chromium plate. 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 process of this invention for preparing a nickel plate receptive to a decorative metallic deposit, characterized by the presence of microporous areas and microcracked areas over substantially the entire surface of said metal plate, comprises affixing to a basis material bearing a conductive metal sur-

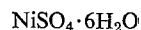
face a stratum of particles having a particle size of about 0.05–15 microns and a density on said conductive metal surface of about 100–5,000,000 particles/cm.²; and depositing in said stratum of particles a nickel layer having a high tensile stress of at least about 8,400 kg./cm.² and an effective thickness less than the maximum thickness of said stratum of particles thereby forming a matrix wherein said particles are retained affixed to said surface in fixed position in said nickel layer, and at least some of said particles intercept the surface of said nickel layer.

The basis material which may be treated according to this invention may include a basis metal such as iron, steel, brass, bronze, copper, zinc, aluminum, magnesium, nickel, etc., either pure or in the form of alloy. The preferred basis metal to be plated in accordance with this invention may be steel, zinc, or brass and most preferably steel, zinc, or brass which has been first plated with a conductive deposit such as a plate of bright nickel, typically preceded by a first plate of copper, bronze, or semi-bright nickel.

Other basis materials which may be treated by the process of this invention may include plastics and resins including acrylonitrile-butadiene-styrene, acetals, acrylics, alkyds, allyls, amines, cellulose, chlorinated polyethers, epoxys, furanes, fluorocarbons, isocyanates (urethanes), polyamides (nylons), phenoxys, phenolics, polycarbonates, polyesters, polyethylenes, polypropylenes, silicones, polystyrenes, polyvinyls, and copolymers, etc. of these materials. When the basis material to be treated by process of this invention is a plastic or resin, the surface thereof will be treated as by deposition thereon of a conductive deposit, such as a nickel deposit.

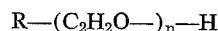
The basis material may be immediately treated after disposition of such plate or it may be water rinsed; or it may be rinsed, dipped in aqueous acid solution such as 0.5%–10%, say 2%, by weight of sulfuric acid prior to further treatment. The so-treated material may be dried or it may be further treated as is. If drying has been permitted, the conductive surface may be cleaned as by cathodically treating in alkaline cleaner followed by rinsing in water or dipping in an acid solution before further treatment.

The basis metal may preferably be given a first nickel flash or strike by immersion in a nickel strike bath containing 88–196 g./l., say 119 g./l. hydrochloric acid (37%) and 100–200 g./l., say 135 g./l. nickel chloride NiCl₂·6H₂O and 100–200 g./l., say 135 g./l. of



for 1–4, say 2 minutes at 15° C.–30° C., say 20° C. and 2.5–7.5, say 4 a.s.d. The nickel strike may be deposited in thickness of 0.6–1.8 microns, say 1.5 microns.

The so-flashed basis metal may then preferably be given a first plate of copper, preferably from an acid-copper plating bath. Acid copper baths may commonly contain 150–120 g./l., say 220 g./l. of CuSO₄·5H₂O and 45–110 g./l., say 60 g./l. concentrated sulfuric acid together with additives including e.g. polyoxyethanols



or aldehydes, or thiazolidine thione, etc. Typically these baths may be operated at a current density of 0.5–15 a.s.d., say 7 a.s.d. at temperature of 15° C.–30° C., say 20° C., to yield an acid copper plate of 0.8–24 microns, say 12 microns. The term "a.s.d." as used herein means "amperes per square decimeter."

A typical bath may for example contain 220 g./l. CuSO₄·5H₂O; 60 g./l. H₂SO₄; 0.02 g./l. Cl⁻; 0.02 g./l. gamma,gamma'-thiodipropyl sulfonate; 0.1 g./l. 2,4,7,9-tetramethyl-4,7-di(hydroxy, polyethoxy)decyne-5; and 0.001 g./l. N-(2-hydroxyethyl) ethylene thiourea.

Plating with this illustrative acid copper bath for 10.6 minutes at 21° C. and 5 a.s.d. may yield a plate of 12 microns thickness.

Nickel plating baths which may be employed in the practice of this invention in forming plate on the surface of the basis material may include various electrodeposition baths. Typical baths may include those indicated below, all values being grams per liter (g./l.), except for the pH which is electrometric.

A typical Watts bath which may be used in practice of this invention may include baths containing the following components in aqueous solution:

TABLE I

Components	Minimum	Maximum	Preferred
Nickel sulfate, hydrated.....	200	500	300
Nickel chloride, hydrated.....	30	80	45
Boric acid.....	35	55	45
pH.....	3	5	4.0

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

TABLE II

Components	Minimum	Maximum	Preferred
Nickel sulfamate.....	330	400	375
Nickel chloride, hydrated.....	15	60	45
Boric acid.....	33	55	45
pH.....	3	5	4.0

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

TABLE III

Components	Minimum	Maximum	Preferred
Nickel sulfate, hydrated.....	300	500	400
Boric acid.....	35	55	45
pH.....	3	5	4.0

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

TABLE IV

Components	Minimum	Maximum	Preferred
Nickel sulfamate.....	300	400	350
Boric acid.....	35	55	45
pH.....	3	5	4.0

A typical pyrophosphate-type which may be used in practice of the process of this invention may include the following components in aqueous solution:

TABLE V

Components	Minimum	Maximum	Preferred
Sodium pyrophosphate hydrated..	50	80	65
Nickel sulfate, hydrated.....	80	160	120
Sodium bisulfite.....	1.5	2.5	2
Sodium citrate, hydrated.....	50	70	60
Citric acid.....	10	20	15
Sodium chloride.....	20	40	30
Ammonia (28%).....	30	60	50
pH.....	7.5	9	8.5

A typical fluoroborate-type bath which may be used in the practice of the process of this invention may include the following components in aqueous solution:

TABLE VI

Components	Minimum	Maximum	Preferred
Nickel fluoroborate, hydrated....	250	400	300
Nickel chloride, hydrated.....	15	60	30
Boric acid.....	15	30	20
pH.....	2	4	3.0

It will be apparent that the above baths may contain components in amounts falling outside the preferred minima and maxima set forth, but that most satisfactory and

economical operation may normally be effected when the components are present in the baths in the amounts indicated.

The plating baths may further contain brighteners or other additives such as sodium saccharate or wetting agents. High-foaming wetting agents such as sodium lauryl sulfate may be particularly useful when employed in conjunction with mechanical agitations; and low-foaming agents such as sodium dialkylsulfosuccinates may be particularly useful when employed in conjunction with air agitation.

In practice of this invention, the basis material preferably bearing a first plate (of e.g. copper) and a nickel or duplex nickel plate, may be further treated by affixing thereto a stratum of particles having a particle size of about 0.05–15 microns.

Typically the particles may be finely-divided, naturally-occurring or artificially prepared materials. They may be spherical, chunky, angular, ovular, elongated, platelet-shaped, etc. Preferably they may be flat, i.e. have two dimensions substantially greater than the third dimension. The preferred particles may be platlets.

Typical particulate materials which may be employed may include talc; kaolin; wax; graphite; sulfides such as molybdenum disulfide and tungsten disulfide; pigments including barytes, chromium-cobalt green and cobalt-aluminum blue and oxides such as silica and alumina; particles of plastic e.g. polymers or copolymers of styrene, butadiene, acrylonitrile, vinyl acetate, vinyl chloride, etc.; diatomaceous earths; powdered aluminum; activated carbon; silicates e.g. sodium silicate; carbonates, e.g. calcium carbonate; carbides; sulfur; etc., or mixtures of these materials.

There may also be present other additives such as polar organic compounds, e.g. amides, amines, long-chain alcohols, acetylenics, etc., to enhance the properties of adhesion, corrosion, inhibition, or dispersion, preferably there may also be present a tertiary alkyl amine containing 18–22 carbon atoms in the alkyl group, typified by Primene 81R, marketed by Rohm and Haas.

Application of particles may be effected by contacting the basis material with particles. The particles may be blown over the surface of the conductive metal surface of the basis material. The basis material may be dipped into a bed, preferably a fluidized bed of particles i.e. particles suspended in an upflowing stream of gas. Affixing of particles may be effected by electrostatic or electrophoretic techniques on the basis metal piece. If desired, the basis metal may be wet to assist deposition thereon and adherence thereto of the particles.

The preferred particles may be used in the form of a bath i.e. a suspension, emulsion, dispersion, or latex of the solid or semi-solid particles in a fluid, preferably a liquid. In one preferred embodiment, the particles may be particles of solid suspended in a liquid in concentration as low as 0.001%, typically, 0.1–2%, and preferably about 0.5%. Outstanding results may be obtained by use of baths containing 0.1%–2% particles.

Typically the particles in the bath may be from commercially available materials: for example, talc may be obtained having particles ranging in size up to about 7 microns. 0.01%–2% of talc may be added to water and dispersed as by milling in a ball mill or in a Waring Blender or by stirring. Similar techniques may be employed to disperse wax, pigments, kaolin, etc.

The fluid, typically aqueous medium, in which the particles may be suspended may be water, but preferably is a bath having a composition substantially similar to the bath immediately preceding from which the basis material may have been removed after treatment, e.g. a water-rinse bath or a nickel-plating bath.

Air, mechanical, or ultrasonic agitation may be used to maintain the particles in suspension. Additives such as suspending agents including surfactants, dispersants, thixotropes, emulsifiers, etc., e.g. alginates, lignosulfonates,

gelatin, etc., may be present, and if desired, electrolytes including sodium sulfate, heavy metal salts, acids, etc.

When the bath is a latex bath, it may be formed from various resins. Illustrative resins which may be present in latices used in the instant invention include resins containing non-aromatic unsaturation in the repeating unit of the molecule formed from:

(a) Diene compositions including butadiene typically natural rubber; isoprene i.e. 2-methyl butadiene; chloroprene i.e. 2-chloro-butadiene; pentadiene-1,3; etc.

(b) Acrylate compositions including acrylate and methacrylate esters such as methyl acrylate; methyl methacrylate; ethyl acrylate; ethyl methacrylate; propyl acrylate; etc.

(c) Acrylonitrile compositions including acrylonitrile; methacrylonitrile; ethacrylonitrile; etc.

(d) Vinyl compositions including vinyl chloride; vinyl acetate; 1-chloro-propene-1; styrene; o-, m-, and p-methyl styrenes; etc.

(e) Olefin compositions including ethylene; propylene; butylene; etc.

Typical compositions may include those formed from more than one of the above types, such as from two components including butadiene-styrene; butadieneacrylonitrile; methyl acrylate-styrene; etc. or three components (terpolymers) including e.g. acrylonitrile-butadiene-styrene; etc. Most preferably polymers of the noted compositions may be used in the form of copolymers with e.g. other noted compositions.

The above compositions may be modified and typically carboxylic-modified i.e. the molecule containing aliphatic unsaturation may be modified by the addition thereto of a carboxylic acid group. Typically this may be effected e.g. by reacting the composition with maleic anhydride in order to form carboxylic groups on the polymer molecule or by hydrolyzing a —CN group to a carboxyl group.

It is a feature of the latices which may be employed in practice of the process of this invention that they may be readily available from natural sources e.g. natural rubber latex or that they may readily be formed by dispersing synthetic compositions in aqueous media e.g. butadiene-styrene polymer latices.

Illustrative specific commercially available synthetic latices which may be used in practice of this invention include:

(a) A water-based acrylic polymer latex having a non-ionic emulsifier, a pH of 7, and an average particle size of 0.16 micron (such as that sold under the trademark Hycar 2601 by B. F. Goodrich Chemical Co.);

(b) A water-based copolymer of butadiene-styrene-carboxylic modified latex (i.e. a latex wherein butadiene-styrene copolymer is modified by the inclusion of —COOH groups), including a synthetic emulsifier, a pH of 9, and an average particle size of 0.16 micron (such as that sold under the trademark Pliolite 491 by Goodyear Industrial Products Co.);

(c) A water-based hydrocarbon resin latex having a nonionic emulsifier, a pH of 8.8, and a maximum particle size of 1 micron (such as that sold under the trademark Piccopale N-3 by Pennsylvania Industrial Chemical Corporation);

(d) A water-based vinyl acetate polymer latex having a nonionic emulsifier, a pH of 4.0-5.5, and an average particle size of about 1 micron (such as that sold under the trademark Plyamul 40-370 by Reichold Chemical Co.);

(e) A water-based vinyl acetate polymer latex having an anionic emulsifier, a pH of 3.5-5.5, and an average particle size of 0.5 micron (such as that sold under the trademark Gelva TS-30 by Shawinigan Resins Corp.);

(f) A water-based copolymer of butadiene-styrene 50/50 latex having a synthetic emulsifier, a pH of 9.6, a non-staining anti-oxidant, and an average particle size of 0.6 micron (such as that sold under the trademark Pliolite 176 by Goodyear Industrial Products Co.);

(g) A water-based vinyl acetate polymer latex having a pH of 8.0, and an average particle size of 0.16 micron (such as that sold under the trademark Dow 700 by Dow Chemical Co.);

(h) A water-based vinyl acetate polymer latex having a pH of 4.0-5.0, an anionic emulsifier, and a particle size of 0.05-3 microns (such as that sold under the trademark CL-102 by Celanese Corp. of America);

(i) A water-based copolymer of vinylidene chloride acrylonitrile 85/15 latex having an anionic emulsifier, a pH of 6.0-7.0, and an average particle size of 0.2 micron (such as that sold under the trademark Saran Latex F122 A15 by Dow Chemical Co.);

The preferred latices may be in the form of nonconductive latices in aqueous medium, typically containing 30-60%, say 40%, resin in the aqueous medium. Commonly these latices may be characterized by the presence of colloidal-size particles, typically less than about one micron and commonly of the order of 0.0005-0.2 micron. The most highly preferred latices which may be used in practice of this invention to permit attainment of the preferred chromium plate containing microcracked areas and micro-porous areas over substantially the entire area of the chromium plate include the carboxylic-modified butadiene copolymer latices containing particles of an average size of up to about 1 micron. Typical of such latices is b. supra sold under the trademark Pliolite 491 in which the average particle size may be about 0.16 micron. Other latices may include vinylidene chloride copolymer latices such as the copolymer with acrylonitrile, as i. supra sold under the trademark Saran Latex F122 A15 in which the average particle size may be about 0.2 micron. A preferred latex may for example be a polyvinyl chloride latex containing 0.5% by weight of polyvinyl chloride having a nominal particle size about 0.16 micron, such as that sold under the trademark Dow 700 (g. supra). Additives including dispersants etc. may be present.

Typically the particles may be employed in the form of an aqueous dispersion having the following composition:

TABLE VII

	Parts by weight		
	Minimum	Maximum	Preferred
Particles.....	0.001	5	0.5
Fluid.....	95	100	99.5
Additive(s).....	0.00005	0.01	0.01

A preferred bath in the form of a dispersion which may be employed may include:

TABLE VIII

	Parts by weight		
	Minimum	Maximum	Preferred
Talc.....	0.005	5	0.5
Water.....	95	100	100
Dimethyl oleamide.....	0.00005	0.10	0.01
Sodium lignosulfonate.....	0.00005	0.10	+0.01

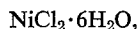
Application of the particles onto the metal surface may preferably be effected by dipping the metal surface in an aqueous bath containing said particles. Dipping may be effected, preferably at ambient temperature of 10° C.-40° C., and the surface may be retained therein for time sufficient to inundate the surface, typically 5-60 seconds, preferably about 30 seconds. Moderate agitation in this step may be preferred.

The surface may then be removed from the bath bearing a stratum of particles which cling evenly distributed thereon—probably held in place by surface tension and adsorptive forces. The particles may be affixed to the surface by these forces and may be uniformly distributed thereover. Typically there may be 100–5,000,000 particles on each square centimeter of surface, and commonly 5,000–2,000,000 particles/cm.².

The surface so-attained may, if desired, be allowed to dry, or it may be water-washed, or it may be further processed as is, e.g. bearing a thin film of adherent liquor.

The surface bearing the stratum of affixed particles may then be further treated. There may then be deposited on said surface and in said stratum, a conductive nickel layer having a high tensile stress of at least about 8,400 kg./cm.² and an effective thickness less than the maximum thickness of said stratum of particles thereby forming a matrix wherein said particles are retained affixed to said surface in fixed position in said conductive metal surface, and at least some of the particles intercept the surface of said conductive nickel layer.

The matrix-bearing surface may be immersed in a nickel plating bath. According to one embodiment, high tensile stress nickel may be obtained by immersing the basis metal bearing said plate(s) into an electroplating bath containing (a) nickel ion, (b) nickel chloride



(c) nickel fluoborate $\text{Ni}(\text{BF}_4)_2$, (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 noted in Table IX.

TABLE IX

Components	Minimum	Maximum	Preferred
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.....	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 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 high tensile

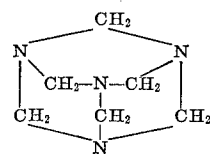
stress outer nickel plate may be deposited may contain an additive heterocyclic chemical compound having at least two nitrogen atoms in an otherwise carbocyclic ring structure. These heterocyclic compounds may be monocyclic, dicyclic, bicyclic, tricyclic, etc. although commonly they may be monocyclic. 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-isoimidazole (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-pyrimidine (i.e. 4-pyrimidine), isoindazole (i.e. benzopyrazole), 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.

Inertly substituted 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.

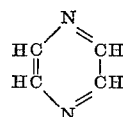
Typical illustrative compounds which may be employed in practice of this invention may be the following: s-triazine, u-triazine, v-triazine, pyridazine, pyrimidine, indole, isobenzazole, pyrimidine, isoindazole, cinnoline, quinazoline, naphthyridine, pyrido[3,4-b]pyridine, pyrido[3,2-b]pyridine, pyrido[4,3-b]pyridine,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

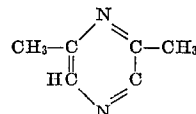
- (I) hexamethylene tetramine
- (II) pyrazine
- (III) 2,6-dimethyl pyrazine
- (IV) 1:1'ethylene 2:2'dipyridinium dichloride



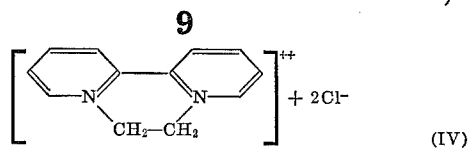
(I)



(II)



(III)



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 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 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-Senderoff Contractometer. Normally the high tensile stress 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.

According to a second embodiment, high tensile stress

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nickel may be deposited on said surface and in said stratum by immersing the basis metal into an electroplating bath consisting essentially of (a) nickel ion, (b) nickel sulphate NiSO₄·6H₂O, (c) ammonium ion, (d) boric acid, and (e) a water-soluble primary brightener.

Typically such baths may be as noted in Table XIII.

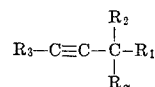
TABLE XIII

Components	Minimum	Maximum	Preferred
Ni ⁺⁺	13	90	20
NiSO ₄ ·6H ₂ O.....	60	400	90
NH ₄ ⁺	1.6	13.5	4
H ₃ BO ₃	13	45	30
Brightener.....	0.2	0.8	0.6
Temperature, ° C.....	20	65	55
pH.....	5	6	5.5
Agitation.....	Mechanical	and/or air or solution pumping	
c.d. (asd.).....	0.5	10	4

The brightener which may be employed in practice of this invention may include water-soluble acetylenic compounds.

Water-soluble acetylenic compounds which may be employed in this invention may be particularly characterized by a highly nucleophilic triple bond which is free from steric hindrance and thus has a clear and unimpeded path in approaching the cathode.

The preferred water-soluble acetylenic compounds which may be employed in the process of this invention to produce nickel deposits may include alpha-substituted acetylenic compounds having the formula



in which each of R₁ and R₂ may be substituents selected from the group consisting of hydrogen, alkyl, alkenyl, alkenyl, hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkenyl groups, and R₁ and R₂ may together be a carbonyl oxygen; R₃ may be a substituent of the group consisting of hydrogen, halogen, alkyl, alkenyl, alkenyl, hydroxy-substituted and alkoxy-substituted alkenyl and alkenyl groups, and substituted-alkyl groups having the formula



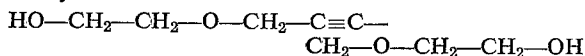
in which each of R₄ and R₅ may be substituents selected from the group consisting of hydrogen, alkyl, alkenyl, alkenyl, and hydroxy-substituted and alkoxy-substituted alkyl, alkenyl, and alkenyl groups, and when R₁ and R₂ together are carbonyl oxygen, R₃ may be an aryl group, including hydroxy and alkoxy and alkyl-substituted aryl; each of R₄ and R₅ may be substituents selected from the group consisting of hydroxy, alkoxy, carboxy-substituted alkoxy, formoxy, alkanoxy, halogen and polyoxy groups and R₄ may also be an amino group including alkyl and aryl substituted amino group when R₁ and R₂ together form a carbonyl oxygen and R₃ is an aryl group. Where R₃ is a substituted-alkyl group having the above-illustrated formula, the acetylenic compound may be termed an α,α'-disubstituted acetylenic compound, since both carbon atoms vicinal to the same acetylenic bond contain either the same or a different functional group.

The compounds listed in Table XIV are illustrative of the water-soluble acetylenic compounds which may be used in practice of the process of this invention.

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TABLE XIV

2-butyne-1,4-diol
 1,4-di-(β -hydroxyethoxy)-2-butyne
 1-(β -hydroxyethoxy)-2-butyne-4-ol
 1,4-diacetoxy-2-butyne
 3-butyne-1,2-diol
 [3-methyl-1-butyne-3-ol]
 3-methyl-1-pentyn-3-ol
 2-propyn-1-ol
 2,5-dimethyl-1-octen-3-yn-5-ol
 3-methyl-1-nonyn-3-ol
 2,4-hexadiyne-1,6-diol
 1-methoxy-2-propyne
 3-methoxy-3-methyl-4,6-heptadiyne
 3-ethoxy-3,5,7-trimethyl-1-octyne
 1-formoxy-2-propyne
 1-acetoxy-2-propyne
 3-methyl-1-nonyn-3-yl-acetate
 phenyl-propiolamide
 phenyl-propiol-N-phenylamide
 phenyl-propiol-N,N'-dimethylamide
 3-methyl-1-butyn-3-yl acetate
 1-chloro-6-methoxy-2,4-hexadiyne
 3-chloro-3-methyl-4-hexyne
 1-bromo-2-propyne
 1,2-di-(β -hydroxyethoxy)-3-butyne
 3-(β -hydroxy- γ -chloropropoxy)-3-methyl-4-pentyne
 3-(β - γ -epoxypropoxy)-3-methyl-4-pentyne

Those acetylenic compounds which may be employed in the instant invention include those containing at least one hydroxy moiety, and most preferably those which contain two hydroxy moieties, e.g. the β -hydroxy-ethyl ether of 2-butyne-1,4-diol, i.e. 1-(β -hydroxy-ethoxy)-4-hydroxy-2-butyne, and preferably the bis(β -hydroxy ethyl ether) of 2-butyne-1,4-diol, i.e. 1,4-bis(β -hydroxyethoxy)-2-butyne:



Other water-soluble primary brighteners which may be used in practice of this step of the process may include other stress-producing primary brighteners such as N-2,3-dihalopropenyl pyridinium halide including those wherein the pyridinium may be substituted with e.g. 2,4,6-trimethyl or 3,5-dimethyl or 2-amino or 3-sulfo as well as corresponding quinolinium or isoquinolinium compounds. Typical of such brighteners may be N-,2,3-dichloropropenyl pyridinium chloride.

The brightener may be present in the bath in effective amounts of 0.002 g./l.-0.5 g./l., preferably 0.005 g./l.-0.10 g./l., say 0.01 g/l-0.05 g./l.

Deposition of the high stress nickel deposit in accordance with this aspect of the invention may be carried out at 20° C.-65° C., say 55° C. for 0.5-2 minutes, say 1 minute, to permit attainment of a nickel plate having a thickness of 0.1-1.0 microns, say 0.75 microns when plating with a current density of 0.5-10 amperes per square decimeter (a.s.d.), say 4 a.s.d.

The so-deposited plate may typically be bright and may have a stress of at least about 8400 kg./cm.² preferably about 8400-1400 kg./cm.² and typically 9800 kg./cm.².

According to a third embodiment, a high tensile stress nickel-cobalt alloy may be deposited on said surface and in said stratum. Typically this may be carried out by deposition from the following typical preferred bath:

TABLE XV

Components	Minimum	Maximum	Preferred
Ni ⁺⁺ +Co ⁺⁺	52.5	130	67.2
Ni ⁺⁺	52	108	60.9
Co ⁺⁺	0.5	30	6.3
NiSO ₄ ·6H ₂ O.....	200	400	240
NiCl ₂ ·6H ₂ O.....	30	75	30
CoSO ₄ ·7H ₂ O.....	2.5	145	15
H ₂ BO ₃	30	50	30
(NH ₄) ₂ SO ₄	0.5	1.0	0.75
Formaldehyde.....	1.5	45.0	2.5
Nickel formate.....	30	60	45

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Preferably plating may be effected over 0.12-2 minutes, say 1 minute at 20° C.-65° C., say 55° C. at 1-10 a.s.d. say 5 a.s.d. to yield a nickel-cobalt alloy plate of 0.02-3 microns, say 0.2 micron thick.

The high tensile stress nickel (including nickel cobalt alloy) is characterized by a tensile stress of at least about 8400 kg./cm.² and preferably by a tensile strength which is higher than the tensile stress. Thus the high tensile stress nickel will normally be substantially of any crack pattern including microcracks or gross cracks.

Plating may typically be carried out to produce a conductive high-tensile stress nickel layer preferably having an effective thickness less than the maximum thickness of the stratum of particles whereby said particles are retained in fixed position in the conductive or nickel layer and at least some of said particles penetrate the surface of the layer. Typically the effective thickness may average 0.02-3 microns, preferably 0.2 micron. There will thus be formed a matrix of particles in a nickel layer of metal, i.e. a heterogeneous matrix deposit. Microscopic inspection of the matrix deposit may readily reveal that the particles may be retained in fixed position in a matrix of the nickel layer. It will also be observed (as by dark field illumination in a microscope or by the Dubpernell test) that the particles may traverse the conductive layer and may be observed above the upper surfaces thereof.

Inspection of the stratum of particles in which the highly stressed nickel conductive layer has been deposited will clearly indicate that when the nickel layer is deposited in effective thickness less than the maximum thickness of the stratum of particles, there may be formed a matrix wherein the particles affixed to the metal surface are retained in fixed position in the nickel layer and at least some of the particles intercept the surface of the nickel layer. When the particles in the nickel layer are substantially spherical particles having more-or-less uniform size, the resulting matrix cross-section may appear to be essentially as set forth in FIG. 1 of the drawing. Here the effective thickness of the conductive layer may be 50%-60% of the thickness of the stratum of particles and the particles more-or-less uniformly intercept the surface of the conductive layer in which they are retained in fixed position.

In FIG. 2, there is shown a typical illustrative cross-section through the surface of a conductive nickel layer having an effective thickness less than the maximum thickness of the stratum of particles. In this FIG. 2, the particles are heterogeneously sized; as will be apparent, varying proportions of different sized particles intercept the surface of the conductive layer in which the particles are retained in position.

In FIG. 3, is shown a typical cross-section of a matrix formed by first affixing a plurality of flat platelets of heterogeneous size to the basis metal and thereafter depositing a conductive nickel layer in the stratum. As will be apparent from inspection of this FIG. 3, the effective thickness of the conductive layer is less than the actual thickness of the stratum of particles, i.e. in spite of the bridging effect, the upper portion or surface of at least some of the platelet particles is not covered by the deposited conductive layer. It will be noted however that the actual thickness of the conductive layer may be greater than the actual thickness of the stratum by as much as half the average width of the typical platelet particle.

Typically the actual thickness of the conductive layer which yields an effective thickness less than the maximum thickness of the stratum of particles may vary from typically about 20%-30% of the thickness of the stratum to as much as 200% of the thickness of the stratum. For example, when the particles are irregular or highly porous, the actual thickness of the conductive layer may be as little as 20%. When the particles are substantially spherical and uniformly sized, the actual thickness of the conductive layer may be 50%-60%. When the particles are heterogeneously sized platelets, the actual thickness of the conductive layer may be 50%-200% or more typ-

ically 100% of the maximum thickness of the stratum of particles.

Under each of these conditions, the effective thickness of the conductive nickel layer is less than the maximum thickness of the stratum of particles, i.e. the conductive layer forms a matrix wherein the particles of said stratum are retained in fixed position in the conductive layer and at least some of said particles traverse the conductive layer and intercept or penetrate the surface of said conductive layer. In each of these embodiments, it will be observed that the particles in the matrix remain affixed to and appear to be in contact with the metal surface of the basis material.

The product so-prepared may typically thus include a nickel plate (receptive to a metal plate, such as a decorative chromium plate, characterized by the presence of microporous or microcracked areas over substantially the entire surface of said chromium plate) comprising a basis material bearing a conductive metal surface, and affixed thereto 100-5,000,000 particles/cm.², each particle having a size of about 0.05-15 microns, said particles being fixed in a matrix containing a nickel layer having a high tensile stress of at least about 840/kg./cm.², at least some of said particles traversing said nickel layer and intercepting the surface thereof.

The basis metal plated with matrix plate, as hereinabove set forth, may then be further plated with a decorative metal deposit, typically chromium. Chromium plating may be effected at temperature of 30° C.-60° C., say 43° C., and current density of 5-50 a.s.d., say 10 a.s.d., for 0.5-15 minutes, say 5 minutes, from a bath containing 100-500 g./l., say 250 g./l. of chromic acid and 1-5 g./l., say 2.5 g./l. of sulfate ion, typically derived from sodium sulfate. Other components including other chromium plating catalysts, e.g. fluoride or silicofluoride, self-regulating strontium ion-containing compositions, fume suppressants, etc. may be present in the chromium plating bath.

The chromium plate prepared by the process of this invention may be obtained in thickness of at least 0.02 micron, typically in decorative thickness of less than about 1 micron, and may be further particularly characterized by its bright decorative appearance, its high corrosion-resistance, and by its microcracked and microporous structure. The chromium plate, which lies over the matrix plate containing particles which may partially protrude above or intercept the surface of the conductive layer, may possess microcracking and microporosity over substantially the entire area of its surface.

The microcracked surface area of the chromium plate prepared by the process of this invention may be found to have at least 100 microcracks per linear centimeter at 40 mm. from the high current density end of a standard Hull Cell panel plated with 10 amperes for 5 minutes at 43° C., compared to 5-10 microcracks per inch for the same chromium on the typical prior art nickel plate. This unexpectedly high degree of microcracking is sufficient to obtain microcracked areas over all thicknesses of chromium plated in the high and intermediate current density areas. The high degree of microcracking extends sufficiently over the surface of the chromium plate so as to be essentially contiguous with the microporous areas which are characteristic of the low current density areas of the chromium plate on the matrix surface.

This product may be inspected under a microscope and found to contain a microporous surface in the low current density areas of the standard Hull Cell panel. Typically it may possess a plurality of pores, typically about one hundred to two or three million (at a chromium thickness of less than about 0.5 micron), more-or-less uniformly distributed over the surface of the metal. Chromium deposited, on e.g. a nickel plate, prepared by the process of this invention may thus be found to contain microporous areas or microcracked areas over the entire surface. Because of the presence, over all areas of the chromium

plate, of microperforated areas (i.e. either microporous areas or microcracked areas), it is possible to attain the novel benefits herein set forth.

When chromium plating is applied to the heterogeneous matrix-stratum described herein unexpected benefits are derived. Other factors being constant, the cracking of a chromium plate will depend on its thickness. Such factors as concentration of chromic acid, concentration of catalyst materials, temperature of plating, etc.; all have an effect. It is characteristic of prior art chromium deposits generally that no cracking appears throughout the first stage of deposition, up to about 0.5 micron. As the thickness is increased in the undesirable second stage, e.g., in the range of 0.5-1.0 microns, gross cracking may develop; in the undesirable third stage, e.g. about 1.0-1.5 microns, spangle-type cracking, i.e., microcracking interspersed in gross cracking, may develop. In the fourth stage, microcracking alone may develop. The undesirable intermediate stages, i.e., stages two and three, may be objectionable in appearance in the as-plated condition and particularly so after the initiation of corrosion has emphasized the presence of the cracks. Micropores and microcracks are not objectionable because the fineness of structure is not perceived by the eye except with aid of magnification. Furthermore the presence of these microperforations over the entire plate, permits attainment of the outstanding corrosion-resistant properties hereinafter set forth.

It has been unexpectedly found in the practice of this invention that microporosity is produced in stage one and microcracking is facilitated so that the undesirable stages two and three, i.e., gross and spangle-type cracking, do not appear. Thus a final plated chromium part may have microporosity where low current densities occur and microcracking in higher current density areas with no objectionable gross cracking or spangle.

The preferred thickness of the bright decorative electroplated chromium plate may be 0.02-5.0 microns, say 0.5 micron. The degree of microcracking (attained at thickness greater than about 0.5 micron) over a typical matrix nickel plate may be at least 100 microcracks per linear centimeter.

While there has been described specific examples in connection with the preferred embodiment of this invention, it will be obvious to those skilled-in-the-art that various changes and modifications may be made therein without departing from the invention.

EXAMPLE 1

In this example, which represents a preferred example of a complete system including plates deposited in accordance with the process of this invention, the basis metal was a piece of cold rolled steel typical of those used in automotive applications. The metal was vapor degreased, cleaned anodically in an alkaline cleaner, water rinsed, dipped into acid-dip, and water rinsed. Nickel strike was then applied electrolytically from a standard nickel bath to yield a nickel strike of 1.5 microns.

After a further water rinse, the metal was given a 17.5 micron thick coating of bright acid copper in 10.6 minutes from the following bath:

Acid copper bath

Component:		
CuSO ₄ ·5H ₂ O	-----g./l---	225
H ₂ SO ₄	-----g./l---	54
Cl-	-----g./l---	0.005
2-mercaptothiazoline	-----g./l---	0.001
N-(2-hydroxyethyl)ethylene thiourea	---g./l---	0.001
gamma, gamma'-thio dipropyl sulfonate (Na salt)	-----g./l---	0.02
di - 2 - (7 - sulfonate naphthyl)methane (Na salt)	-----g./l---	0.4
2,4,7,9 - tetramethyl - 4,7 - di(hydroxyl, polyethoxy)decyne-5	-----g./l---	1.0
Temperature °C.	-----	21
Current density (a.s.d.)	-----	5

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The acid copper plate may then be water-rinsed, acid dipped in 2% sulphuric acid, water rinsed, and then plated in a semi-bright nickel bath having the following formulation:

Semi-bright nickel bath

Component:		
NiSO ₄ ·6H ₂ O	g./l.	300
NiCl ₂ ·6H ₂ O	g./l.	60
H ₃ BO ₃	g./l.	45
Potassium 6-sulfo- <i>ω</i> -propyl coumarin	g./l.	0.54
Sodium dihexyl sulfosuccinate	g./l.	0.06
pH		4.2
Current density (a.s.d.)		5
Time (minutes)		11
Temperature (°C.)		63
Air agitation		

The semi-bright plate was obtained in thickness of 12.5 microns after 11 minutes.

The semi-bright nickel plate was directly transferred into the bright nickel bath wherein it was plated under the following conditions:

Bright nickel bath

Component:		
NiSO ₄ ·6H ₂ O	g./l.	300
NiCl ₂ ·6H ₂ O	g./l.	60
H ₃ BO ₃	g./l.	45
Butyne 1,4-diol	g./l.	0.1
Tris-cyanoethyl-2-thiohydantoin	g./l.	0.002
Sodium dihexyl sulfosuccinate	g./l.	0.06
pH		4.2
Current density		5
Time (minutes)		7
Temperature (°C.)		60
Air agitation.		

The bright nickel plate was obtained in thickness of 7.5 microns after 5 minutes. The plate was brilliant and ductile.

The bright nickel plate was then water rinsed and dipped into an aqueous bath containing the following:

Particle bath

Component:	Parts (g./l.)	
Talc (Mistron Manomix brand, having a maximum particle size of 6 microns and a median particle size of 1 micron)		0.2
Hydroxy ethyl cellulose dispersant		0.01
Tertiary-alkyl (having 18-21 carbon atoms) amine.—Primene 81R brand of Rohm and Haas		0.005

The plate bearing on the surface a layer of said bath was then water rinsed and then plated in the following high tensile stress bath:

High tensile stress nickel bath

Component:		
Ni ⁺⁺	g./l.	20
NiSO ₄ ·6H ₂ O	g./l.	90
NH ₄ ⁺	g./l.	4
H ₃ BO ₃	g./l.	30
Butyne diol-1,4	g./l.	0.6
Temperature, °C.		55
pH		5.5
C.d. (a.s.d.)		4
Agitation-Air		4
Time (minutes)		1

The high tensile stress nickel which is deposited over 1 minute is obtained in thickness of 1 micron. The tensile stress was found to be 8400 Kg./cm.².

This nickel was water washed and the system was chromium plated under the following conditions:

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Chromium plating bath

Component (as made up):

CrO ₃	g./l.	203
So ₄ =(from SrSO ₄)	g./l.	1.8
SiF ₆ =(from Na ₂ SiF ₆)	g./l.	1.6
Na ₂ Cr ₂ O ₇ ·2H ₂ O	g./l.	203
Time (seconds)		40
Cdd. (a.s.d.)		30
Temperature (°C.)		49

The chromium so deposited was obtained in thickness of 0.25 microns.

This sample was subjected to the standard CASS corrosion test and the rating was 10/10 after 69 hours. In this test, the rating is given as a pair of numbers wherein the first number indicates the degree of basis metal corrosion and the second number indicates the appearance. In each case over a scale of 0-10, the higher numbers indicate a better rating; and values greater than 7-8 may be acceptable.

A series of comparative control examples was carried out as follows:

EXAMPLE 2

In this control example, the basis metal was treated as in Example 1 except that the plate was not dipped in the talc bath. The CASS rating was 10/5.

EXAMPLE 3

In this control example, the basis metal was treated as in Example 1 except that the plate was not dipped in the talc bath and the plate was not plated with high tensile stress nickel. The CASS rating was 7/6.

EXAMPLE 4

In this control example, the basis metal was treated as in Example 1 except that the first acid copper plate was omitted. The CASS rating was 8/8.

EXAMPLE 5

In this control example, the basis metal was treated as in Example 1, except that the basis metal was not given a plate of acid copper, was not dipped in talc, and was not given a plate of high stress nickel. The CASS rating was 6/6.

EXAMPLE 6

In this example, the basis metal was treated as in Example 1, except that the high tensile stress nickel bath was as follows:

Component:	Amount (g./l.)
Ni ⁺⁺	150
NiCl ₂ ·6H ₂ O	150
NiBF ₄	450
Butyne diol-1,4	0.2
Saccharin	0.25

The CASS rating was 10/10.

EXAMPLE 7

In this example, the basis metal was treated as in the process of Example 1, except that the high tensile stress nickel bath was as follows:

Component:		
Ni ⁺⁺	g./l.	60.9
Co ⁺⁺	g./l.	6.3
N ⁺⁺ +Co ⁺⁺	g./l.	67.2
NiSO ₄ ·6H ₂ O	g./l.	240
NiCl ₂ ·6H ₂ O	g./l.	30
CoSO ₄ ·7H ₂ O	g./l.	15
H ₃ BO ₃	g./l.	30
(NH ₄) ₂ SO ₄	g./l.	0.75
Formaldehyde	g./l.	2.5
Ni formate	g./l.	45
pH	g./l.	3.7
Current density (a.s.d.)	g./l.	4
Air agitation.		

The plate obtained at 60° C. over 1 minute was 1 micron thick and it has a CASS rating of 10/10.

From the above examples, it will be apparent that the novel process of this invention produces results which are outstanding with respect to corrosion resistance as measured by the CASS test. For example, Example 1 yields a CASS rating of 10/10 which is outstanding. In contrast, the system of Example 4 which omits the acid copper plate has a CASS rating of only 8/8. Thus it may be observed that the pressure of the acid copper bath increased the corrosion resistance of the plate of Example 1. That this is unexpected may be observed by a comparison of Example 5 (using a semi-bright nickel, a bright nickel, and chromium) with Example 3 also containing a first plate of acid copper. The CASS ratings of Examples 3 and 5 are 7/6 and 6/6, respectively.

From inspection of Example 4, it will be apparent that the use of the high stress nickel yields a CASS rating of 8/8 which is better than e.g. Example 5.

The experimental Examples 1, 6, and 7 each gave an outstandingly high CASS rating of 10/10 which is totally unexpected. It must be noted that these examples contain only about 20 microns of total nickel on the acid copper. By comparison, typical prior art systems (similar to Example 5, but containing 1.5-2 times more nickel, typically 30 microns) has only a CASS rating of 6/6. Thus it is totally unexpected that the systems of Examples 1, 6 and 7 should permit attainment of these outstanding results.

Although this invention has been illustrated by reference to specific embodiments, modifications thereof which are clearly within the scope of the invention will be apparent to those skilled-in-the-art.

We claim:

1. A process for preparing a nickel plate receptive to a decorative chromium metal deposit, characterized by the presence of microporous areas and microcracked areas over substantially the entire surface of said chromium metal plate, which comprises:

affixing to a basis material bearing a conductive metal surface a stratum of particles having a particle size of about 0.05-15 microns and a density on said ductive metal surface of about 100-5,000,000 particles/cm.²;

and then depositing in said stratum of particles a nickel layer free of said particles having a high tensile stress of at least about 8,400 kg./cm.², and an effective thickness less than the maximum thickness of said stratum of particles;

thereby forming a matrix wherein said particles are retained affixed to said surface in fixed position in said nickel layer, and at least some of said particles intercept the surface of said nickel layer.

2. The process as claimed in claim 1 wherein the basis material bears a conductive metal surface containing nickel.

3. A process as claimed in claim 1 wherein the basis material bears a conductive metal surface containing copper.

4. A process as claimed in claim 1 wherein the particles are affixed to a basis material bearing a conductive metal surface by dipping said basis material bearing a conductive metal surface into a fluidized bed of particles suspended in an up-flowing stream of gas.

5. A process as claimed in claim 1 wherein the particles are affixed to a basis material bearing a conductive metal surface by dipping said basis material into liquid containing particles of solids suspended in the liquid in a concentration of 0.1%-2% by weight.

6. A process as claimed in claim 1 wherein the particles are affixed to a basis material bearing a conductive metal surface by dipping said basis material into a liquid containing particles of solids suspended in said liquid in a concentration of 0.01%-2% and containing particles of talc ranging in size up to about 7 microns.

7. The process as claimed in claim 1 wherein the density on the conductive metal surface of the particle is 5,000-2,000,000 particles/cm.².

8. The process as claimed in claim 1 wherein the high tensile stress nickel layer is prepared from a nickel plating bath containing acetylenic compounds.

9. The process as claimed in claim 5 wherein the bath is a latex bath.

10. The process as claimed in claim 5 wherein the bath contains dimethyl oleamide and sodium lignosulfonate.

11. A nickel plated article receptive to a decorative chromium metal deposit characterized by the presence of microporous areas and microcracked areas over substantially the entire surface of said chromium metal plate prepared by:

affixing to a basis material bearing a conductive metal surface a stratum of particles having a particle size of about 0.05-15 microns and a density on said conductive metal surface of about 100-5,000,000 particles/cm.²;

and then depositing in said stratum of particles a nickel layer free of said particles having a high tensile stress of at least about 8,400 kg./cm.², and an effective thickness less than the maximum thickness of said stratum of particles;

thereby forming a matrix wherein said particles are retained affixed to said surface in fixed position in said nickel layer, and at least some of said particles intercept the surface of said nickel layer.

12. A nickel plated article as claimed in claim 11 containing a decorative chromium metal deposit characterized by the presence of microporous areas and microcracked areas over substantially the entire surface of said chromium metal plate.

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