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3,268,424

METHOD OF DEPOSITING A CORROSION RESISTANT COMPOSITE NICKEL ELECTROPLATE

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This application is a continuation-in-part of our co-pending applications, Serial No. 45,285, filed July 26, 1960, now Patent No. 3,152,971; Serial No. 45,287, filed July 26, 1960, now Patent No. 3,152,973; Serial No. 262,191, filed March 1, 1963; Serial No. 262,199, filed March 1, 1963; and Serial No. 262,200, filed March 1, 1963.

This invention is for improvements in or relating to decorative nickel electroplating, and more particularly relates to (1) the electrodeposition of sub-microscopic textured to macroscopic satin textured fine-grained nickel plate from semi-bright and bright nickel plating baths containing dispersed therein certain bath-insoluble particles hereinafter described, and (2) to the exceptional corrosion resistance of these deposits when overlaid with a thin chromium plate.

The decorative fine-grained nickel deposits of this invention have various degrees of brightness, or uniform smokiness, or of uniform satin-sheen depending mainly on the concentration and particle size of the dispersed fine powders in the semi-bright or bright nickel electroplating baths, the concentration of the nickel brighteners, the degree of agitation of the cathode or the solution, the brightness and smoothness of the metal surfaces plated upon, and the thickness of the plate applied, and these decorative nickel plates of various degrees of sub-microscopic, microscopic, and macroscopic satin texture and luster when over-laid with a final thin chromium plate provide exceptionally outstanding corrosion protection to the underlying metal.

We have found that the very improved decorative nickel deposits of this invention may be produced by dispersions in semi-bright and bright nickel electroplating baths of certain bath-insoluble fine powders consisting of the compounds of metals having incomplete inner electron shells, such as the metals of the transition series, the metals of the lanthanide or rare earth series, and of the actinide series. For example, excellent powders for the purpose of this invention are, the bath-insoluble compounds of metals of the transition series, such as nickel oxalate, cobalt oxalate, the ferrites, such as nickel ferrite (NiFe_2O_4), cobalt ferrite, barium ferrite, manganese ferrite, gadolinium ferrite, iron cobalt ferrite, and including magnetic iron oxide (FeFe_2O_4), chromites such as ferrous chromite (FeCr_2O_4), barium chromite, nickel chromite, cobalt chromite; the bath-insoluble compounds of the lanthanide or rare earth series such as the rare earth oxalates, rare earth phosphates, rare earth silicides, rare earth sulfides, rare earth fluorides; the oxides, silicates, titanates, zirconates and stannates of lanthanum, neodymium, praseodymium, yttrium, samarium, didymium, and the unseparated rare earth mixtures, such as rare earth oxide, rare earth stannate, rare earth silicate, rare earth titanate, rare earth zirconate; the bath-insoluble compounds of the common members of the actinide series including, for example, thorium tetrafluoride, thorium fluoroborate, thorium fluosilicate, thorium sulfide, thorium silicate (thorite), thorium titanate, thorium zirconate, uranium tetrafluoride, and uranium sulfides.

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Previously in co-pending application Serial 45,287 the excellent results obtained with the alkaline earth oxalates, that is with calcium, strontium and barium oxalates, were described, and in co-pending application Serial 45,285 the excellent results obtained with iron silicide and certain oxides such as silica, ceric oxide, ferric oxide, aluminum oxide, etc., were described. In Serial 262,200 the beneficial results of certain bath-insoluble stannates and phosphates were described. In Serial 262,199 the beneficial results of certain bath-insoluble titanates, zirconates and silicates were described. Also in Serial 45,286 the results of certain silicates were described. We have now found that the alkaline earth oxalates when added as powders to the semi-bright and bright nickel acidic nickel electroplating baths form mixed oxalates with nickel. That is, some fine nickel oxalate is precipitated out, and also some nickel oxalate is formed by co-precipitation and adsorption on the surface of the alkaline earth oxalates. Since the nickel ion is present in high concentration in the acidic nickel baths, the formation of the very slightly soluble nickel oxalate is favored by the law of mass action. Nickel oxalate itself as a nickel oxalate powder gives excellent results in producing very high corrosion protection. The nickel oxalate particles can be formed as precipitates directly in the bath by adding such soluble oxalates as sodium, potassium, lithium, or magnesium oxalates, and other soluble oxalates, sodium ing oxalic acid itself. Of these soluble oxalates, sodium and magnesium oxalates are preferred for the direct formation of nickel oxalate precipitate in the bath, which is finely dispersed by agitation, especially by air agitation of the bath.

It has also been found that the oxalates of cobalt and manganese give good results. It was further found that the rare earth oxalates give extremely good results in very low to very high concentrations of powder. Cerous oxalate powder is very good as is mixed "rare earth oxalate" which is not expensive. The rare earth oxalates of neodymium and didymium (the latter is a natural mixture of neodymium and praseodymium), are also not expensive. Neither is yttrium or lanthanum oxalate excessively expensive in technical grades and they give excellent results. Scandium oxalate and the rare earth oxalates of samarium and gadolinium and praseodymium also give good results but these oxalates are much more expensive at present than cerous oxalate or lanthanum oxalate or neodymium oxalate. Europium, terbium, dysprosium, erbium, holmium, ytterbium, thulium, and lutetium oxalates are very expensive when separated as individual rare earths, and it is therefore preferred to use technical grades such as "rare earth oxalate," cerous oxalate, lanthanum oxalate, neodymium oxalate, didymium oxalate.

It is to be understood that in many cases of the oxalates mentioned, such as cerous oxalate, cobalt oxalate, etc., nickel oxalate is also formed to a certain extent as a fine precipitate when the other oxalates are added to the nickel baths. The nickel oxalate as well as the other water-insoluble oxalates are least soluble in the acidic nickel baths at the higher pH values of the nickel baths, that is, at pH values of 4 to 6.

These oxalate precipitates and powders especially nickel oxalate and the rare earth oxalates produces exceptionally highly corrosion resistant plate when given the usual final over-lay plate of about 0.01 mil (0.25 microns) of chromium plate. Even concentrations of about 0.5 gram/liter of these fine oxalate powders make possible improved corrosion protection when the decorative plates obtained from these baths are given a final chromium plate of thickness less than about 0.2 mil (5 microns).

The oxide powders, for example, are not quite as effective as the oxalates at low concentrations.

The maximum improvement in corrosion protection in the less accessible recessed areas of articles is attained, however, when about 10 to about 100 grams/liter of the fine powders are present as dispersions in the nickel baths, and further increase in concentrations of powder does not improve the already exceptional corrosion resistance when a final thin chromium plate is applied. With the higher concentrations of powder the plates become more hazy up to a point where further increase in concentration of powder produces no further change in appearance of the nickel plate at a given nickel plate thickness on a given base at a given rate of agitation of the bath or the cathode and with a given brightener concentration in the nickel bath. The oxide powders (especially ferric iron oxide powder alone or mixed with fine silica), generally produce less haziness than the other powders. As high as at least about 300 grams/liter of fine powders can be dispersed in the bath.

The average particle diameter (herein sometimes referred to as "particle size") of the finely powdered bath-insoluble materials should preferably not be greater than about 5 microns. The use of material of particle size less than about 5 microns is preferred and is advantageous, with the most preferred particles size averaging about 0.02 to about 3 microns. However, agglomerated particles may originally have larger particle size than 5 microns but with air agitation in the nickel bath the larger agglomerates are reduced to ultimate particle size of 5 microns and under by the air agitation of the bath. Agitation is usually necessary to keep the fine powder suspended in the baths during plating. Air agitation or mechanical agitation including ultrasonic agitation of the baths can be used. Air agitation is preferred.

Analysis of the nickel plates from an air agitated bright nickel bath containing superfine cerous oxalate powder of particle size of about 0.02 to 5 microns in concentrations of about 5 to 50 grams/liter shows usually less than about 0.5% by weight of the powder present in the nickel plate. Microscopic examination of the surface of the plate shows an extremely uniform finely pitted surface which consists of micro-inclusions and micro-pits. Calculations and microscopic examinations indicate that the number of micro-inclusions and micro-pits per sq. cm. of surface is of the order of 10^6 . The calculations are based on ultimate particle size. However, in many cases the particles are present as small agglomerates in the nickel plate. This textured plate has excellent adhesion, for example, to nickel, ferrous, copper and brass surfaces similar to that obtained when the nickel bath contains none of the powdered material. The leveling of the bright nickel plate is not decreased by the presence of the finely powdered additives. The throwing and covering power of the agitated bright nickel bath with the suspended powders is about the same as without the fine powders present. It has been found that in plating articles with recessed areas and with shelf areas using particles of the preferred particle size, no objectionable roughness is obtained on the areas on which settling can occur.

The fine bath-insoluble powders plate out as uniform dispersions in the semi-bright and bright nickel plate and thereby cause sub-microscopic (with the finest particles of 0.01 to about 0.05 micron size) to micro-inclusions and sub-microscopic to microscopic-pitting in the surface of the nickel plate. That is, at any given instant surface of the semi-bright or bright nickel plate has distributed over its surface multitudinous fine particles in various stages of being imbedded in the surface and causing sub-microscopic and microscopic pitting, and with the thinnest plates (flashes or strikes) the pitting is mostly sub-microscopic becoming more microscopically visible with thicker plating. When the usual chromium plate of about 0.01 mil (0.25 micron) chromium is applied to these sub-microscopic to microscopic particles textured sur-

faces a very fine favorable porosity pattern is developed in the chromium plate which is the key to the extraordinary corrosion protection afforded to the underlying metal by this composite nickel-chromium plate. With the very fine porosity pattern that is developed in the thin chromium plate there is obtained the very favorable condition of tiny cathode areas, the chromium surrounding the multitudinous tiny anodes (the sub-microscopic and microscopic pits) which results in very weak corrosion currents with very low anodic current densities in the corrosive environments. Thus, the penetration of the corrosion pits toward the underlying basis metal is very greatly diminished. There is also the possibility that due to the chemical reaction of the partially imbedded oxalate particles with the chromic acid of the chromium bath that the chromium plate may have some chromium chromate inhibitor formed in the micro-pits which would also be favorable to minimize the start of anodic attack. However, from the results obtained under prolonged severe corrosion exposure it is clear that it is the tiny cathode areas (chromium) surrounding the multitudinous tiny anode (nickel) areas that are responsible for the remarkable corrosion protection afforded by the thin chromium plated sub-microscopic-to-macroscopic-textured fine grained nickel deposits of this invention.

These textured nickel deposits give the best appearance and corrosion protection results when plated on top of semi-bright sulfur-free nickel or bright nickel deposits. It is best and also simpler to use the regular semi-bright or bright nickel plating baths for most of the plate and to use the minimum of the textured nickel plate required to obtain the desired appearance and corrosion resistance because the textured nickel plating bath requires added control due to the presence of the dispersed particles, and also because the best corrosion protection results are obtained in this way.

The mechanism by which the particles plate out is not completely understood, but it is thought that the adsorption of hydrogen ions and nickel ions by the particles would give the particles a positive charge and in this way they would tend to plate out. Under the powerful reducing conditions at the nickel cathode it may be possible that the particles which are not semi-conductors become semi-conductors by partial reduction. Irrespective of the mechanism of the plating out of these particles into the nickel plate, it is amazing how readily these particles plate out in a surprisingly uniform manner in semi-bright and bright nickel plates. The plating out of the fine particles starts immediately and in the bright nickel plating baths there is evidence that the first layers of nickel plated out actually contain somewhat higher concentrations of the fine powder than the subsequent ones. Also, the first layers may cause more micro-stress cracking in the thin chromium than the subsequent layers.

Before technical grade powders are used commercially they should always be checked first in small scale tests such as in 1-4 liter baths before being added to large baths because certain harmful impurities such as metallic powders or too coarse particles may be present which will cause rough plate, especially on shelf areas, but otherwise technical grade fine powders normally produce results similar to those obtained from the use of high purity grades of the same particle size and structure. This is especially true of the preferred rare earth oxalates.

In general, bright or semi-bright nickel plating baths of the Watts, sulfate, high chloride, sulfamate, fluoroborate, bromide, fluoride, benzene, methane or ethane sulfonic acids, etc., or mixtures, can be used. While boric acid is the buffer usually preferred, other buffers, such as formates, acetates, succinates or citrates may also be employed, alone or in combination, with beneficial results for control of an optimum pH value.

The pH of the baths may be from about 2 to 6, though the preferred pH value are from about 3.5 to 5.5. The

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temperature of the baths can be from room temperature to at least 80° C., though in general a temperature of about 55° C. to about 65° C. is preferred.

The best addition agents or brighteners to achieve the semi-bright and bright nickel plating conditions necessary to obtain the lustrous textured nickel after the addition to the bath of the afore-mentioned powders are the following: the sulfur-containing brighteners including aromatic and unsaturated aliphatic sulfonic acids, sulfonamides and sulfonimides, such as the benzene- or naphthalene-sulfonic acids, p-toluene sulfonamide, benzene sulfonamide, o-benzoyl sulfimide, vinyl sulfonic acid, vinyl benzene sulfonic acid, allyl sulfonic acid, 2-butyne-1, 4-disulfonic acid, o-sulfobenzaldehyde, etc.; the addition agents which produce semi-bright sulfur-free nickel plate such as formaldehyde, chloral hydrate, bromal hydrate, coumarin, butyne diol, adducts of butyne diol, used alone or in combination; combinations of unsaturated addition agents containing unsaturated linkages such as



$\text{C}=\text{C}$, $\text{C}=\text{N}$, $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$, with organic sulfur-containing brighteners, organic sulfon-compounds, and combinations of the latter with small concentrations of amines, such as quinaldine, polyamines or unsaturated amines such as N-allyl isoquinolinium bromide, or other quaternaries of pyridines or quinolines or isoquinolines.

Cobalt and iron can be present in the nickel bath as cobalt or ferrous sulfates, chlorides, bromides, sulfamates or fluoborates in concentrations as high as at least 40 grams/liter, yielding nickel alloy plates containing concentrations of cobalt and/or iron up to 50% or a little more and it is to be understood that, except when the context requires otherwise, the expression "nickel plate" as used herein covers such nickel alloy plates.

Surface active agents may be present in the baths, but are not usually necessary in the air agitated baths.

The maximum increase in lustrous sheen is obtained when the fine powders are used in the agitated full bright nickel plating baths such as the air-agitated bright nickel plating baths possessing good leveling properties. Less luster is obtained when the nickel baths contain only a carrier type brightener such as benzene or naphthalene sulfonic acids, p-toluene sulfonamide, benzene sulfonamide or o-benzoyl sulfimide. In the latter cases the luster is flatter. This is also true when the semi-bright sulfur-free type of addition agent such as formaldehyde, coumarin, chloral hydrate or bromal, is used solely with the fine powders, and with these semi-bright addition agents it is usually best to use the ultra-fine particle size powders of less than about 1.5 micron particle size.

The sub-microscopic to macroscopic textured nickel deposits of this invention accept chromium plate like regular nickel plate, and in general only the usual thicknesses of final chromium layer need be used, that is 0.25 microns (0.01 mil) though thicknesses of 2.5 or 5 microns may be used. Besides, the decorative nickel finish as such, or with the usual final chromium finish, the sub-microscopic to macroscopic textured nickel plate can be given a rhodium, silver, tin, brass, bronze, copper, gold, or tin-nickel (65-35) alloy or other final thin coating.

When the ultra-fine particles of about 0.01 to 0.1 micron size particles are used in the semi-bright and bright nickel electroplating baths, it is difficult to see the included particles in cross-sections of the nickel plate even at the highest magnification of the light microscope. However, on the surface of the plate using strong light it is possible to just see the microscopic pitting effect of these sub-microscopic particles as a faint Tyndall effect. The thinner the plate that is deposited on a bright

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surface, the more difficult is it to readily distinguish any difference between the appearance of the textured deposit and the bright plate obtained without the particles present. With increasing thickness of the deposit and with increasing concentrations of the fine particles, the micro-inclusions and micro-pitting can be more readily discerned. Thus, in the examples of baths of this invention, the lower concentrations of powder of about 0.5 gram/liter to about 50 grams/liter are best for obtaining the brightest plate from the bright nickel baths, and can thus be used best for thin plates of about 0.01 to about 0.2 mil thickness on top of regular bright nickel or semi-bright nickel plate to obtain after the final thin chromium plate very high corrosion protecting bright plate. Using the CASS and Corrodokote accelerated corrosion tests, many cycles are passed with only 0.6 or 0.8 mil of regular bright nickel or semi-bright nickel that is given a thin plate, for example 0.01 to 0.1 mil, from the baths illustrated in the above examples, and a final 0.01 mil chromium plate. Whereas, with regular bright nickel alone of the same total plate thickness and the same final thin chromium plate, not one cycle is passed.

The nickel brighteners that produce a very high leveling and brilliance as, for example, those given in U.S. 2,647,866 (August 4, 1953) and U.S. 2,800,440 and 2,800,442 (July 23, 1957) will produce the highest brilliance with the powders dispersed in these bright nickel baths. For less luster, the higher concentrations of the powders (100-300 grams/liter) can be used with just the organic sulfon-compounds present as brighteners. These latter brighteners such as o-benzoyl sulfimide, or o- or p-toluene sulfonamide naphthalene mono-, di-, or tri-sulfonic acids, etc., can be used in concentrations ranging from about 0.1 gram/liter to saturation.

Mixtures with other fine non-metallic bath-insoluble powders of average particle size of about 5 microns and less can be used. For example, nickel oxalate powder with fine silica powder or fine nickel carbonate powder, or fine calcium fluoride powder. An extremely excellent combination of fine powders is nickel oxalate with silicon dioxide and nickel oxalate with barium oxalate or strontium oxalate or strontium sulfate mixed also with silicon dioxide. These combinations are best made as follows. Soak up about a one percent to a saturated solution of sodium oxalate, magnesium oxalate or oxalic acid solution in a porous silicon dioxide powder preferably of the type of Philadelphia Quartz brand Quso microfine silica or similar silica powder which has an ultimate particle size of about 0.02 microns but which is usually in the agglomerated form of bolls of about 1.5 micron average particle size, and which is very porous and absorbent. Then drain off excess liquid from the silica powder and add to the semi-bright or bright nickel electroplating bath, preferably the air agitated type. The silica besides its role as a very beneficial and effective powder also functions to modify the formation and growth of the nickel oxalate precipitate, leading to very fine nickel oxalate impregnated silica as well as separate nickel oxalate fine precipitate. Also if the silica is impregnated with barium or strontium chloride and then mixed with nickel oxalate powder excellent results are obtained, and likewise if the silica is impregnated with sodium oxalate and then this and barium chloride or strontium chloride is added to the bright plating baths as a solution or soaked up first in silica powder, excellent corrosion resistance results are obtained with an over-layer chromium plate of less than about 0.2 mil thick. Other brands of fine silica which form agglomerates of average particle size of at least 5 microns tend to break down in agitated baths to agglomerates around 1.5 micron size also give good results. These mixed powders of silica with nickel oxalate, or of silica mixed with barium or strontium sulfate and nickel oxalate of average particle sizes of 5 microns and less give optimum results when used in the ratio of 10 to 50 grams/liter of fine

silica, 0.5 to 20 grams/liter of nickel oxalate and 1 to 20 grams/liter of barium sulfate or strontium sulfate. Mixtures of the fine silica with cerous oxalate and/or magnetic iron oxide, give very good results. Optimum results are obtained with 20 to 50 grams/liter of the silica with 5 to 50 grams/liter of magnetic iron oxide. Mixtures of cerous oxalates or rare earth oxalates with magnetic iron oxide powder give very good results especially with 1-20 grams/liter of rare earth oxalates to 5 to 50 grams/liter of magnetic iron oxide.

To achieve the highest possible corrosion protection results with the textured decorative nickel plate of this invention on complex shaped articles such as many zinc die-cast articles, for example, rear view mirror holders, intricate light housings, steel bumpers, hub caps, and grilles, it is best to use duplex or dual nickel underneath the textured nickel deposit. Thus, the total nickel deposit would consist of semi-bright sulfur-free nickel followed by regular bright nickel followed by a thin textured nickel deposit of this invention. The latter being used as thin plate (0.01 to about 0.2 mil) if the highest brilliance is desired, or as a thicker plate with more powder in the bath and only the sulfonamide or sulfonic acids present as brighteners to obtain a more subdued brightness if desired. If between the semi-bright sulfur-free nickel and the regular bright nickel, a thin plate (0.02 to 0.1 mil) of higher sulfur-content (as nickel sulfide), nickel plate (0.1 to 0.2% sulfur) than the bright nickel plate (0.05 to 0.08% sulfur), is used, then with this tri-nickel plate with a final textured nickel plate of this invention before the top thin chromium plate, even the thinnest total nickel plate (0.3 mil) in deeply recessed articles stands up extremely well in very corrosive atmospheres. When ductile copper plate is used under nickel plate that has a final coating of the textured decorative nickel plate of this invention, then the copper plate also helps in the total corrosion resistance unlike the case when copper is used as a substitute for part of the bright nickel thickness in deposits of copper-bright nickel and the usual 0.01 mil final chromium. It is believed that this beneficial effect of copper is also due to the tiny cathode areas developed in the final thin chromium plate, which in turn is due to the fine favorable porosity pattern developed in the thin final chromium plate as a result of its being deposited over a decorative nickel surface containing multitudinous sub-micro to micro-inclusions and sub-micro to micro-pits of the order of 10^6 per sq. cm.

A particularly desirable and extremely corrosion resistant composite plate is formed by electroplating the nickel plate of this invention on the upper layer of the composite nickel coating described and claimed in co-pending application Serial No. 103,296, filed April 17, 1961, now Patent No. 3,090,733, which is assigned to the assignee of this invention. This composite plate comprises a lower nickel plate having an average thickness of about 0.15 mil to about 1.5 mils and an average sulfur content less than about 0.03%, a first overlying electroplate of nickel, or nickel-cobalt alloy containing at least about 50% nickel and having a thickness of about 0.005 mil to about 0.2 mil and an average sulfur content of about 0.05% to about 0.3%, a second overlying layer of nickel or nickel-cobalt alloy containing at least about 50% nickel having a thickness of about 0.15 mil to about 1.5 mils and an average sulfur content of about 0.02% to about 0.15%, the second overlying layer containing a lower percentage of sulfur than said first overlying nickel electroplate and a higher percentage of sulfur than said lower nickel plate, an overlying layer of the nickel plate of this invention, and a top or upper layer of chromium having a thickness less than about 5 microns. In this composite plate, the fine grain nickel plate of this invention may vary from a thin layer of 0.01 mil to the thicker plate of at least 0.1 or 0.2 mil and such composite plates give extremely excellent corrosion resistance.

Besides the air agitated and mechanical agitated baths for rack plated work, the powders of this invention can be used very effectively in bulk or barrel bright nickel plating. The agitation of the solution caused by tumbling of the articles to be plated is often sufficient to keep the fine particles suspended and dispersed in the bright nickel bath. When such bulk bright nickel plated articles such as fasteners, screws, etc., are given a final chromium plate, outstanding corrosion protection is obtained compared to any previous conventional barrel bright nickel plating.

Below are listed examples of baths of this invention. It is to be understood that other inorganic bath compositions may be used and other brighteners, though one of the preferred class of brighteners is the organic sulfoncompounds. Air agitation of the baths is preferred, as already mentioned. When mechanical agitation of the work or the solution is used that is more vigorous than regular air agitation, less particles are co-deposited in the semi-bright and bright nickel electroplates, and less particles are left adhering to the surface.

Example I

	Grams/liter
25 Nickel oxalate (av. particle size 5 microns and less) -----	10-100
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	200-300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	40-120
H_3BO_3 -----	40
30 o-Benzoyl sulfimide -----	1-4
p-Toluene sulfonamide -----	1-2
Allyl sulfonic acid -----	1-4
2-butyloxy-1,4-diethane sulfonic acid -----	0.05-0.2
pH 3.5-5.5, temp. 50°-70° C.	
35 Air agitation.	

Example II

Nickel oxalate -----	1-50
Silica powder (Quso brand) -----	30-50
40 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	200-300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	40-80
H_3BO_3 -----	40
Benzene sulfonamide -----	2-3
Allyl sulfonic acid -----	1-4
45 N-allyl quinaldinium bromide -----	0.003-0.01
pH 4-6, temp. 50°-70° C.	
Air agitation or mechanical agitation.	

Example III

50 Rare earth oxide (av. particle size 5 microns and less) -----	0.5-20
Cerous oxalate (av. particle size 5 microns and less) -----	0.5-100
55 $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	200-300
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	40-120
H_3BO_3 -----	40
o-Benzoyl sulfimide -----	1-4
Benzene sulfonamide -----	1-2
60 Allyl sulfonic acid -----	1-4
2-butyloxy-1,4-diethane sulfonic acid -----	0.05-0.2
pH 3.5-5.2, temp. 50°-70° C.	
Air agitation.	

Example IV

65 Cerous oxalate (av. particle size 5 microns and less) -----	0.5-100
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ -----	200-300
70 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ -----	30-60
H_3BO_3 -----	40
Bromal and/or chloral hydrate -----	0.05-0.1
Formaldehyde -----	0.02-0.08
pH 3.5-5.2, temp. 45°-65° C.	
75 Air agitation or mechanical agitation.	

Example V

Lanthanum oxalate or neodymium oxalate or rare earth oxalate (av. particle size 5 microns and less) -----	0.5-50	
Magnetic iron oxide -----	0.5-50	5
NiSO ₄ ·6H ₂ O -----	200-300	
NiCl ₂ ·6H ₂ O -----	40-120	
H ₃ BO ₃ -----	40	
o-Benzoyl sulfimide -----	1-4	
Benzene sulfonamide -----	1-2	10
Allyl sulfonic acid -----	1-4	
2-butyloxy-1,4-diethane sulfonic acid -----	0.05-0.2	
pH 3.5-5.2, temp. 50°-70° C.		
Air agitation.		

Example VI

Magnetic iron oxide (av. particle size 5 microns and less) -----	0.5-5.0	
Silica (about 0.015 micron ultimate particle size and av. particle size of agglomerates, 1.5 microns) -----	40-50	20
NiSO ₄ ·6H ₂ O -----	100-250	
NiCl ₂ ·6H ₂ O -----	40-200	
H ₃ BO ₃ -----	40	
o-Benzoyl sulfimide -----	1-4	25
Benzene sulfonamide -----	1-2	
Allyl sulfonic acid -----	1-4	
2-butyloxy-1,4-diethane sulfonic acid -----	0.05-0.2	30
pH 3.5-5.2, temp. 50°-70° C.		
Air agitation for rack work; mechanical agitation for barrel plating.		

Example VII

Didymium oxide -----	1-10	35
Rare earth oxalate (av. particle size 5 microns and less) -----	1-50	
NiSO ₄ ·6H ₂ O -----	0-50	
NiCl ₂ ·6H ₂ O -----	150-300	
H ₃ BO ₃ -----	40	40
Nickel succinate -----	0-15	
o-Benzoyl sulfimide -----	1-4	
Benzene sulfonamide -----	1-2	
Allyl sulfonic acid -----	1-4	
2-butyloxy-1,4-diethane sulfonic acid -----	0.05-0.2	45
pH 3.5-5.2, temp. 50°-70° C.		
Air agitation.		

Example VIII

Thorium fluoride alone and/or mixed with thorium fluoborate, thorium fluosilicate, thorium fluoaluminate, thorium fluotitanate and thorium fluozirconate (av. particle size 5 microns and less) -----	1-50	
NiSO ₄ ·6H ₂ O -----	150-300	
NiCl ₂ ·6H ₂ O -----	150-50	55
H ₃ BO ₃ -----	40	
o-Benzoyl sulfimide -----	1-4	
Benzene sulfonamide -----	1-2	
Allyl sulfonic acid -----	1-4	
2-butyloxy-1,4-diethane sulfonic acid -----	0.05-0.2	60
pH 3.5-5.2, temp. 50°-70° C.		
Air agitation.		

Thorium fluoride when used as the sole powder in the semi-bright and bright nickel electroplating baths makes possible very good corrosion protection results, equal to those given by the oxalate powders. That is, when the nickel deposits obtained from these baths are chromium plated. Also good results are obtained when thorium fluoborate powder is used alone or mixed with thorium tetrafluoride or thorium fluosilicate powder. Magnetic iron oxide (Fe₃O₄) powder causes much more hazy plate than does ferric oxide powder when used in the bright nickel baths, and the corrosion protection results of the composite nickel-chromium plate is superior with the

magnetic iron powder. The least hazy bright plate with excellent corrosion protection results is obtained with the micro-fine silica (Quso brand) powder at 40-50 grams/liter concentration in the bright nickel plating baths. This plate is the least hazy when at least 0.2 mil thick plate is applied, and these bright plates give excellent corrosion protection when given an over-layer of about 0.01 mil thick chromium plate and when the total nickel plate thickness used is about 0.6 to 0.8 mil and consists of conventional semi-bright and/or bright nickel plate with at least 0.01 mil of the final bright nickel plate from the bright nickel bath containing 40 to 50 grams/liter of the fine silica. As already mentioned, combinations of other powders such as nickel oxalate, or strontium or barium sulfate with the silica give excellent corrosion protection results. Also thorium fluoride at 1 to 10 grams/liter, magnetic iron oxide at 0.5 gram/liter and cerous oxalate at 1 to 10 grams/liter give excellent corrosion protection results when used with 40 to 50 grams/liter of the silica and when such nickel plate is given a final chromium plate of less than 0.2 mil (5 microns) thick and especially when the decorative powder containing nickel plate is plated on top of semi-bright and/or bright nickel.

What is claimed is:

1. A method for obtaining improved corrosion resistant composite decorative nickel-chromium plate which comprises the step of electrolyzing and aqueous acidic nickel electroplating bath containing at least one organic nickel brightener capable of producing fine-grained semi-bright to fully bright nickel plate and having dispersed therein about 0.5 to about 300 grams/liter of at least one bath insoluble compound of a metal having an incomplete inner electron shell to thereby form a fine-grained nickel plate, said material in said bath being in the form of a fine dispersion, the major portion of which has an average particle size which is less than about 5 microns and thereafter electroplating on said nickel plate containing said bath-insoluble particles an overlayer of a metal selected from the group consisting of chromium, rhodium, silver, tin, brass, bronze, copper, gold and an alloy consisting of 65 tin and 35 nickel, said overlayer having a thickness less than about 0.2 mil.

2. A method for obtaining improved corrosion resistant composite decorative nickel-chromium plate which comprises the step of electrolyzing an aqueous acidic nickel electroplating bath containing at least one organic nickel brightener capable of producing fine-grained semi-bright to fully bright nickel plate and having dispersed therein about 0.5 to about 300 grams/liter of at least one bath insoluble compound of a metal having an incomplete inner electron shell selected from the group consisting of the ferrites, the chromites, the oxalates of nickel, cobalt, manganese, and yttrium, and at least one of the bath insoluble compounds of the rare earth elements and the elements of the actinide series to thereby form a fine-grained nickel plate, said material in said bath being in the form of a fine dispersion, the major portion of which has an average particle size which is less than about 5 microns, and thereafter electroplating on said nickel plate containing said bath-insoluble particles an over-layer of chromium having a thickness less than about 0.2 mil.

3. A method for obtaining improved corrosion resistant composite decorative nickel-chromium plate comprising the step of electrolyzing (with externally applied current) an aqueous acidic nickel electroplating bath containing dissolved therein at least one organic nickel brightener capable of producing fine-grained semi-bright to fully bright nickel plate and having dispersed in said bath in a concentration of about 0.5 to 300 grams/liter of at least one material selected from the class consisting of bath-insoluble compounds of metals having incomplete inner electron shells selected from the group consisting of the ferrites, the chromites, the oxalates of nickel, cobalt, manganese and yttrium, and the oxalates, phosphates, fluorides, silicides, and sulfides of the rare earth elements, the oxides, silicates, titanates, zirconates and stannates

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of yttrium, lanthanum, neodymium, praseodymium, samarium, didymium, and the unseparated rare earth mixtures, and the bath insoluble compounds of metals of the actinide series, said material being in the form of a fine dispersion, the major portion of the particles of which has an average particle size which is less than about 5 microns, and thereafter electroplating on said fine-grained nickel plate containing said bath-insoluble particles an overlayer of chromium having a thickness of less than about 0.2 mil.

4. A method in accordance with claim 3, wherein the said bath-insoluble material is mixed rare earth oxide.

5. A method in accordance with claim 3 wherein the said bath-insoluble material is didymium oxide.

6. A method in accordance with claim 3 wherein the said bath-insoluble ferrite material is magnetic iron oxide.

7. A method in accordance with claim 3 wherein the said bath-insoluble material is neodymium oxide.

8. A method in accordance with claim 3 wherein the said bath-insoluble material is thorium fluoroborate.

9. A method in accordance with claim 3 wherein the said bath-insoluble material is present in the said nickel bath in a concentration of at least about 10 grams per liter.

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10. A method in accordance with claim 1 wherein said nickel plate is deposited over an electrodeposit consisting essentially of nickel.

11. A method in accordance with claim 1 wherein the said dissolved organic addition agent used in the nickel plating is selected from the group consisting of aromatic and unsaturated aliphatic sulfonic acids, sulfonamides and sulfonimides.

12. A method in accordance with claim 1 wherein said dissolved organic nickel brightener addition agent used in the nickel plating is o-benzoyl sulfinide.

13. A method in accordance with claim 1 wherein said nickel plate overlies an electrodeposit consisting essentially of lustrous nickel plate.

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