

1

3,152,971

ELECTRODEPOSITION OF FINE-GRAINED LUSTROUS NICKEL

Thaddeus W. Tomaszewski, Dearborn, and Henry Brown, Huntington Woods, Mich., assignors, by mesne assignments, to The Udayite Corporation, Warren, Mich., a corporation of Delaware
 No Drawing. Filed July 26, 1960, Ser. No. 45,285
 22 Claims. (Cl. 204-41)

This invention relates to the electrodeposition of nickel with a satin-like appearance directly from aqueous acidic nickel baths. More particularly this invention provides a method for obtaining a fine-grained lustrous satin nickel plate of exceptional corrosion resistance directly from the plating bath.

Satin or brushed finished nickel or chromium plate is normally more expensive than the bright nickel finishes which are obtained with high-leveling, bright nickel plating which require no further polishing or buffing. To obtain the most pleasing satin finishes, dull nickel or dull chromium plate is most often employed, and is subsequently brush finished to obtain the satin lustre. This latter step is expensive, and also decreases the corrosion protection afforded by the satin plate because the brush marks or polishing scratches penetrate appreciably in the plate especially in recessed areas where the plate is thin. For these reasons, that is, expense, and decreased corrosion resistance, satin finished nickel or chromium are not usually used for exterior parts of automobiles or boats.

It is an object of this invention to provide plating baths and methods to produce fine-grained lustrous satin nickel directly from the bath that not only has a very pleasing appearance, but which can be high-lighted by buffing raised area to give beautiful two-tone effects, and which will also provide exceptionally good corrosion protection to the basis metal such as ferrous, aluminum, magnesium, brass, copper and zinc articles.

It has now been found that nickel plating baths normally designated as bright nickel baths, or semi-bright nickel baths can be modified to plate a fine-grained lustrous satin nickel deposit, by incorporating in these baths certain quantities or concentrations of certain finely divided bath insoluble compounds, and plating while these powdered materials are maintained in agitation in these baths. The method of the invention also includes the step of removing from the plated surface any excess powdery material clinging to the plate prior to additional treating steps, such as the preferred final step of chromium plating.

The bath insoluble fine powders which when added to agitated bright nickel or semi-bright nickel plating baths in concentrations from 10 to 500 grams per liter produce a pleasing fine-grained lustrous satin nickel directly from the bath, are certain oxides, carbides, silicides, nitrides, fluorides and sulfides of the group consisting of silicon carbide, boron carbide, titanium carbide, silicon dioxide, manganese oxide, titanium oxide, zirconium oxide, aluminum oxide, ceric oxide, ferric oxide, chromic oxide, boron nitride, calcium fluoride, strontium fluoride, barium fluoride, strontium fluoride, barium fluoride, zinc sulfide, cadmium sulfide, and iron silicide.

It is thought that these materials function in a similar manner to produce the satin plate of this invention because they all have the common property of being semi-

2

conductors and are either bath insoluble or do not decompose in the bath to release components, during electrodeposition or upon standing, which detrimentally affect the plating characteristics of the bath.

These materials must be used in the form of very fine powders with average diameters of less than about 2 microns, otherwise roughness of plate occurs especially on shelf areas of articles where the particles can settle.

The preferred particle size is from about 0.02 to 0.5 micron average diameter, and when used in concentrations of about 10 to 200 grams per liter in agitated bright or semi-bright nickel plating baths produce a smooth fine-grained lustrous satin nickel deposit. The surface of the satin nickel plate obtained under these conditions has approximately 20 million micro-pits per sq. in. as determined by microscopic evaluation at 250X magnification. If the powders are from 0.02 to 0.05 micron ultra-fine particle size, concentrations can be used of about 10 to about 75 grams per liter. If the particle size is about 0.1 to 0.4 micron, then concentrations of about 50 to 200 grams per liter give the best results.

Especially desirable results from a decorative as well as a corrosion resistant standpoint are obtained by the addition of these very fine powders, in concentrations of about 50 to 200 grams per liter to air-agitated bright nickel plating baths such as those described in U.S. 2,647,866, issued August 4, 1953; 2,800,440 and 2,800,442, issued July 23, 1957. Superfine powders of 0.02 to 0.5 micron particle size are especially outstanding in performance. The nickel plate obtained from these agitated bright plating baths containing, for example, about 75-200 grams per liter of these superfine powders, has a semi-bright microscopically-fine pitted surface with a satin smooth sheen of very pleasing appearance. The fine suspended powders tend to cling to the nickel plate, and this effect and the specific physical structure, particle size and shape, and the chemical structure of the powder apparently causes the microscopically-fine pitting effect which converts the normally bright or semi-bright surface to a satin smooth sheen. The uniformity of the sheen is unusual and especially noteworthy in that a 0.2 mil to 2 mil thick or thicker plate can have the same satin appearance. Thus, when contoured articles such as camera parts, ornaments, grilles, automobile dashboards, door handles, marine hardware, etc., are plated, the satin appearance of the plate in the recessed areas (low current density areas) is the same as the plate in the higher current density areas.

Concentrations of the fine powders as high as 500 grams per liter in the bath do not produce any appreciably different results than the optimum concentrations of about 50 to 200 grams per liter. Air agitation or mechanical agitation including ultra-sonic agitation of the baths can be used. The faster or more powerful the agitation and the finer the particle size down to colloidal dimensions, the lower the concentration of fine powder that is necessary, and concentrations as low as 10 grams per liter may be used to obtain a smoky satin finish by using strong agitation and powders having a size of about 0.1 to 0.3 micron or ultra-fine particles having a size of 0.02 to 0.04 micron. Agitation is necessary to keep the fine powder suspended in the bath during plating. In general, however, it is preferred to use from about 50 to 200 grams per liter of very fine powder having a size less than 2 microns in air-agitated baths.

Analysis of a satin nickel plate from an air agitated bright nickel bath containing these superfine insoluble powders of particle size of 0.02 to 0.5 micron in a concentration of about 100-400 grams per liter shows usually not higher than about 2.4% to 2.5% insoluble powder uniformly distributed in the nickel plate. Microscopic examination of the surface of the plate shows an extremely uniform finely pitted surface. This satin plate has excellent adhesion, for example, to ferrous, copper, and brass surfaces just as the plate from the clear nickel bath, and it is quite surprising that these agitated baths containing 100 to 200 grams per liter of these superfine powders give exceptionally smooth to the touch satin plate even in 20 mil and thicker plates, and that practically no gas pitting occurs. The addition of these fine powders in the same concentrations, that is, 50 to 200 grams per liter to agitated plain dull nickel baths, such as the Watts bath, makes the dull nickel plate obtained even duller and more unsightly in appearance.

The throwing power and covering power of the agitated bright nickel baths with the suspended powders is about the same as without the fine powders present. It was found that in plating articles with recessed areas and with shelf areas that no roughness was obtained on the areas on which settling can occur.

The leveling of the bright nickel plate is not decreased by the presence of these fine insoluble powders in the bath. In fact, the leveling seems definitely improved in most cases.

The satin nickel plate obtained from bright or semi-bright nickel plating baths containing these fine powders can easily be polished or buffed to a high lustre, thus, as already mentioned beautiful two-tone effects can readily be obtained by buffing raised or accessible portions of the satin nickel plated object. Also, where a brush satin finish is desired, this can be accomplished by using, for example, 120 or 150 emery polish on the basis metal, then these coarse polishing lines can be seen in the satin sheen nickel, despite the high leveling characteristics of the baths. That is, the coarse polishing lines are only partially smoothed out. Thus, in this way, an excellent brush type satin finish is obtained of higher corrosion protection than when a nickel plate is brushed after plating.

When concentrations of less than about 10 grams per liter of the ultra-fine powders are used in agitated bright or semi-bright nickel plating baths, then the satin appearance of the nickel plate decreases, and the plate has a smoky appearance and has more reflectivity, especially in recessed areas. Thus, it is preferred for the most general satin finish applications as well as corrosion protection applications to use concentrations of the very fine powders greater than about 10 grams per liter.

The use of dispersing agents, peptizing agents in conjunction with the fine powders is often helpful, though not necessary. There are not particular operating troubles because concentrations of 150 grams per liter or higher of these fine powders are used in the bath instead of, for example, 40 to 50 grams per liter of 0.02 to 0.5 micron particle size. The powders of extremely fine or ultra fine particle size of 0.02 to 0.04 micron or less, are generally more expensive, that is, if the great percentage of the particles are of these ultra-fine diameters, however, lower concentration can be used to obtain equivalent effects. Before technical grade powders are used commercially they should always be checked first in small scale tests such as 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. Except for the necessity of this precautionary check, technical grade powders normally produce equal results to those obtained from the use of high purity grades of the same particle size and structure. Also, if the powder is not wetted properly by the nickel bath, it should be checked for freedom of fatty or oily films.

It is important to avoid metallic powders in these baths, for example, poorly cast nickel anodes which might powder during use and disperse nickel particles in the bath definitely can cause roughness, also high concentrations of activated carbon in the bath can cause very undesirably roughness. The carbon from rolled or cast carbon-containing nickel anodes, however, does not usually cause roughness when floating in the baths. High concentrations of iron dissolved as ferrous or ferric iron in the baths do not cause settling roughness or gross pitting effects in the baths even at the pH values of 3.8 to 5.5 although at such pH values dissolved iron tends to precipitate. Zinc or cadmium ions can be present in the baths in concentrations as high as about one gram per liter without detrimentally affecting the plate. Cadmium tends to whiten the plate somewhat. The presence of sodium and magnesium salts are not harmful. Ammonium salts in concentrations higher than about 15 grams per liter is in general not desirable because of reduction of the limiting cathode current density. In general, bright or semi-bright nickel plating baths of the Watts, high chloride, sulfamate and fluoborate baths or mixtures can be used. Also, other buffers besides boric acid may be used, such as formates, citrates, etc.

The pH of the baths may be from about 2 to 6, though the preferred pH values are from about 3.5 to 5.2. The temperature of the baths can be from room to at least 170° F., though in general a temperature of about 130° F. to about 150° F. is preferred.

As already mentioned, the use of these fine insoluble powders does not create a satin sheen nickel plate when added to plain nickel baths that normally produce dull nickel deposits such as the Watts nickel bath. The nickel bath must be a semi-bright or bright nickel plating bath. The best addition agents or brighteners to achieve the semi-bright and bright nickel plating conditions necessary to obtain satin nickel after the addition to the bath of the afore-mentioned powders in concentrations of about 10 to 500 grams per liter are the following: the brighteners of the class of organic sulfon-compounds including aromatic and unsaturated aliphatic sulfonic acids, sulfonamides and sulfonimides, such as benzene sulfonic acids, naphthalene sulfonic acids, p-toluene sulfonamide, benzene sulfonamide, o-benzoyl sulfimide, 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, used alone or in combinations; combinations of the sulfur-free addition agents with those of the organic sulfon-type, and combinations of the latter with small concentrations of amines, such as quinaldine or unsaturated compounds such as N-allyl isoquinolinium bromide and other unsaturated compounds, polyamines, etc.

Cobalt and iron can be present in the nickel bath as the cobalt or ferrous sulfates, chlorides, sulfamates or fluoborates in concentrations as high as at least 40 grams per liter, yielding nickel alloy plates containing concentrations of cobalt and/or iron as high as at least 50%.

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

The maximum increase in satin 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 as those illustrated in Examples 1, 2 below. Less satin lustre, for example that of Example 3, is obtained when the nickel baths contain only the carrier type brightener such as benzene sulfonic acids, naphthalene sulfonic acids, p-toluene sulfonamide, benzene sulfonamide, o-benzoyl sulfimide, etc. In the latter cases the satin lustre is flatter. This is also true when the semi-bright sulfur-free type of addition agent such as formaldehyde, chloral hydrate, or bromal, is used solely with the fine powders, and with these sulfur-free semi-bright addition agents such as those men-

5

tioned, as well as coumarin, it is best to use the ultra-fine particle size powders of less than 0.2 micron particle size, and preferably less than 0.05 micron particle size as determined with the electron microscope. There seems to be a definite improvement in leveling with the semi-bright sulfur-free addition agents when these ultra-fine particle size powders are used. The corrosion protection to steel, aluminum, magnesium, and zinc base die-castings of such chromium plated nickel is greatly improved as shown by repeated passage of such severe accelerated tests as the Corrodokote, with and without a final, sulfur-containing bright nickel overlay plate to give a double layered plate, so-called duplex or dual nickel, of 40 to 60 ratio to 80 to 20 ratio of ultra-fine satin semi-bright sulfur-free nickel to fully bright nickel. Furthermore, it was found that the satin nickel plate obtained from the agitated bright nickel plating baths containing organic sulfon-type addition agents and the fine powders as illustrated in Examples 1, 2 and 3 when plated to a thickness of 1 to 1.5 mils on steel or copper plated zinc die-cast and given the usual 0.01 mil final chromium will itself pass many successive Corrodokote and Cass tests of 20 hours each without any failure. This is due mainly to the development of a very fine favorable porosity pattern in the final thin, 0.01 mil, chromium plate. If the fine powders of this invention are omitted, the resulting full bright nickel plate of the same thickness and with the same thin final chromium plate will fail in only one cycle of 20 hours Corrodokote testing.

There is a strong tendency for the finely-divided powders to remain clinging to the nickel surface after the plated article is withdrawn from the bath and rinsed thoroughly. They often remain clinging even after the usual final chromium plate of 0.005 to 0.05 mil is applied. For such clinging particles which are only slowly soluble in acids or sequestering agents, it was found that a very thin plate from a zinc cyanide bath (about 1 to 3 minutes plating) followed by an acidic or alkaline dip to remove the zinc, also removed the tightly clinging particles. Actually, the particles on the work look like a fine dust and are not really too unsightly even if left on, and they do not hurt the chromium plate. They are readily wiped off with a cloth, or, they can be removed to a certain extent by ultrasonic cleaning.

The satin nickel plate accepts chromium plate like regular nickel plate, and in general only the usual thicknesses of final chromium need be used, that is, 0.01 mil, though thicknesses of 0.1 mil or 0.2 mil may be used. Besides, the final satin nickel finish as such, or with the usual final chromium finish, the satin nickel plate can be given a rhodium, silver, tin, brass, bronze, copper, gold, or tin-nickel (65-35) alloy or other final thin coating. Thin wax, or "soluble-wax," films or clear lacquers greatly decrease finger marking of the final coatings, such as nickel, bronze, silver, brass, etc. Chromium, gold, rhodium, and tin-nickel alloy plate do not need these organic coatings.

In general, for indoor use, satin nickel coatings of only 0.2 to 0.5 mil thickness are needed. For outdoor exposure in industrial or marine atmospheres thicknesses of 1 to 1.5 mils should be used. Also, the satin nickel can be used as the top layer of a double layered or duplex nickel coating, with the undercoat consisting of at least 0.7 mil of semi-bright sulfur-free nickel. This would be for the most severe outdoor exposure as for marine hardware. As already mentioned, however, the corrosion protection to steel, aluminum, magnesium, brass and zinc of the satin nickel with the usual final chromium plate (0.01 mil) even from baths containing organic sulfon-compounds is amazingly superior to the fully bright nickel obtained from the same baths without the fine powders present.

Below are listed some preferred examples of baths for the production of the fine-grained satin nickel plate of this invention. Especially excellent results are produced

6

by Examples 1 to 5. In general, the cathode current density is from 10 to 100 amps./sq. ft. Mixtures of powders may be used, such as zirconium oxide with titanium oxide, aluminum oxide with nickel carbonate, barium fluoride with titanium oxide, etc. It is important that the powders are clean and wetted by the aqueous nickel bath.

Example I

	Conc., grams/liter
Zirconium oxide fine powder (0.03 to 0.3 micron particle size) -----	40-150
NiSO ₄ ·6H ₂ O -----	150-300
NiCl ₂ ·6H ₂ O -----	30-100
H ₃ BO ₃ -----	30-40
p-Toluene sulfonamide -----	1-2
o-Benzoyl sulfimide -----	0.1-2
Allyl sulfonic acid -----	0.5-6
N-allyl quinaldinium bromide -----	0.002-0.01
pH=3.0-5.2.	
Temp.=room to 160° F.	
Air agitation of the bath.	

Example II

	Conc., grams/liter
Titanium oxide superfine powder (0.03 to 0.5 micron) -----	30-200
NiSO ₄ ·6H ₂ O -----	150-300
NiCl ₂ ·6H ₂ O -----	30-150
H ₃ BO ₃ -----	30-40
o-Benzoyl sulfimide -----	1-3
Allyl sulfonic acid -----	0.5-4
2-butyne-1,4-disulfonic acid -----	0.1-10
2-butyne-1,4-diethane disulfonic acid -----	0.05-0.1
pH=2.8 to 5.2.	
Temp.=room to 165° F.	
Air agitation or mechanical agitation.	

Example III

	Conc. grams/liter
Titanium oxide superfine powder -----	30-200
NiSO ₄ ·6H ₂ O -----	75-200
NiCl ₂ ·6H ₂ O -----	30-150
H ₃ BO ₃ -----	30-40
o-Benzoyl sulfimide -----	1-3
p-Toluene sulfonamide -----	1-2
pH=3.0 to 5.0.	
Temp.=room to 180° F.	
Air agitation or mechanical or both.	

Example IV

	Conc. grams/liter
Zirconium oxide ultra-fine powder, 0.02-0.04 micron -----	10-200
NiSO ₄ ·6H ₂ O -----	150-350
NiCl ₂ ·6H ₂ O -----	30-53
H ₃ BO ₃ -----	30-40
Chloral hydrate -----	0.1
Formaldehyde -----	0.04

	$\text{CICH}_2-\overset{\text{CH}_3}{\text{CHOCH}_2}-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$ -----	0.04
60	pH=3.8-5.2.	
	Temp.=room to 150° F.	
	Mechanical or air agitation or both.	

Example V

	Conc. grams/liter
Aluminum oxide superfine optical powder -----	10-200
NiSO ₄ ·6H ₂ O -----	100-300
NiCl ₂ ·6H ₂ O -----	30-75
H ₃ BO ₃ -----	30-40
Allyl sulfonic acid -----	1-3
Benzene sulfonamide -----	1-3
2-butyne-1,4-diethane disulfonic acid -----	0.1-0.2
pH=5.0-5.2.	
Temp.=room to 160° F.	
Air or mechanical agitation.	

Example VI

	Conc. grams/liter
Calcium fluoride microfine powder -----	40-100
NiCO ₃ , BaCO ₃ or SrCO ₃ microfine powder ----	5-150
NiSO ₄ ·6H ₂ O -----	100-300
NiCl ₂ ·6H ₂ O -----	30-100
H ₃ BO ₃ -----	30-40
Ni(BF ₄) ₂ -----	1-3
o-Benzoyl sulfimide -----	0.2-3
p-Toluene sulfonamide -----	1-2
Allyl sulfonic acid -----	1-4
2-butynoxy-1,4-diethane disulfonic acid -----	0.1-0.3

pH=5.0 to 5.2.

Temp.=room to 150° F.

Mechanical agitation.

The satin nickel plate of this invention has about 10 million to about 50 million micro-pits per square inch, as determined by microscopic evaluation at 250× magnification, and in all cases the plate contains a sufficient number of micro-pits to give the plate a microscopic satin appearance.

What is claimed is:

1. A method for electrodepositing a fine-grained lustrous plate which is essentially nickel comprising the step of electrolyzing an aqueous acidic solution of at least one nickel salt selected from the group consisting of nickel sulfate, nickel chloride, nickel fluoborate, nickel sulfamate and mixtures of at least one said nickel salt with up to about 40 grams per liter of at least one salt selected from the group consisting of the sulfates, chlorides, fluoborates and sulfamates of cobalt and iron and at least one soluble organic addition agent capable of producing said fine-grained lustrous plate, said bath containing dispersed therein about 10 to about 500 grams per liter of at least one material selected from the group consisting of silicon carbide, boron carbide, titanium carbide, silicon dioxide, manganese oxide, titanium oxide, zirconium oxide, aluminum oxide, ceric oxide, ferric oxide, chromic oxide, boron nitride, calcium fluoride, strontium fluoride, barium fluoride, zinc sulfide, cadmium sulfide and iron silicide, said material in said bath being in the form of a fine powder, the size of which is less than about 2 microns average diameter, continuing said electrolysis until an adherent decorative nickel plate is formed on said surface, and thereafter electrodepositing thereon an overlayer of a metal selected from the group consisting of chromium, rhodium, silver, tin, brass, bronze, copper, gold and an alloy consisting of about 65% tin and about 35% nickel.

2. A method for electrodepositing a fine-grained lustrous nickel plate comprising the step of electrolyzing an aqueous acidic solution of at least one nickel salt and at least one soluble organic addition agent capable of producing said fine-grained lustrous plate, said bath containing dispersed therein about 10 to about 500 grams per liter of at least one material selected from the group consisting of silicon carbide, boron carbide, titanium carbide, silicon dioxide, manganese oxide, titanium oxide, zirconium oxide, aluminum oxide, ceric oxide, ferric oxide, chromic oxide, boron nitride, calcium fluoride, strontium fluoride, barium fluoride, zinc sulfide, cadmium sulfide and iron silicide, said material in said bath being in the form of a fine powder, the size of which is less than about 2 microns average diameter, continuing said electrolysis until an adherent decorative nickel plate is formed on said surface, and thereafter electrodepositing thereon an overlayer of a metal selected from the group consisting of chromium, rhodium, silver, tin, brass, bronze, copper, gold and an alloy consisting of about 65% tin and about 35% nickel.

3. A method in accordance with claim 2 wherein said fine powder is zirconium oxide.

4. A method in accordance with claim 2 wherein said fine powder is titanium oxide.

5. A method in accordance with claim 2 wherein said fine powder is superfine aluminum oxide optical powder.

6. A method in accordance with claim 2 wherein said fine powder is calcium fluoride.

7. A method for electrodepositing a fine-grained lustrous nickel plate comprising the step of electrolyzing an aqueous acidic solution of at least one nickel salt selected from the group consisting of nickel sulfate, nickel chloride, nickel fluoborate, and nickel sulfamate and at least one soluble organic addition agent capable of producing said fine-grained lustrous plate, said bath containing dispersed therein about 10 to about 500 grams per liter of at least one material selected from the group consisting of silicon carbide, boron carbide, titanium carbide, silicon dioxide, manganese oxide, titanium oxide, zirconium oxide, aluminum oxide, ceric oxide, ferric oxide, chromic oxide, boron nitride, calcium fluoride, strontium fluoride, barium fluoride, zinc sulfide, cadmium sulfide and iron silicide, said material in said bath being in the form of a fine powder, the size of which is less than about 2 microns average diameter, and thereafter plating on said cleaned surface an overlayer of a metal selected from the group consisting of chromium, rhodium, silver, tin, brass, bronze, copper, gold, and an alloy consisting of about 65% tin and about 35% nickel.

8. A method in accordance with claim 2 wherein the metal of said overlayer is chromium.

9. A method in accordance with claim 2, wherein said fine powder is essentially silicon dioxide, and an average diameter of the individual particles thereof is less than about two microns.

10. A composite electroplate on a metal surface susceptible to atmospheric corrosion which comprises a nickel plate with a metallic over-layer, said nickel plate having been electrodeposited from an acidic nickel plating bath containing dissolved therein at least one organic nickel brightener capable of producing semi-bright to fully bright nickel plate, and having dispersed in said bath at least one type of bath insoluble inorganic non-metallic particles the average diameter of the individual particles thereof being less than about 2 microns, an electrodeposited over-layer plate of a metal selected from the group consisting of chromium, rhodium, silver, tin, brass, bronze, copper, gold and an alloy consisting of about 65% tin and about 35% nickel on said nickel plate said over-layer plate being less than about 5 microns in thickness, said type of particles in said nickel bath being selected from the group consisting of silicon carbide, boron carbide, titanium carbide, silicon dioxide, manganese oxide, titanium oxide, zirconium oxide, aluminum oxide, ceric oxide, ferric oxide, chromic oxide, boron nitride, calcium fluoride, strontium fluoride, barium fluoride, zinc sulfide, cadmium sulfide and iron silicide, and said fine particles being present in said nickel bath in an amount sufficient to produce a fine porosity pattern in the said over-layer plate.

11. A composite electroplate in accordance with claim 10, wherein said nickel plate directly overlies an electrodeposit consisting essentially of nickel.

12. A composite electroplate in accordance with claim 10 wherein said dissolved organic nickel brightener is selected from the group consisting of aromatic and unsaturated aliphatic sulfonic acids, sulfonamides and sulfonimides.

13. A composite electroplate in accordance with claim 10 wherein said bath insoluble inorganic non-metallic particles are present in the nickel bath in a concentration of at least about 10 grams per liter.

14. A composite electroplate in accordance with claim 12 wherein said dissolved organic nickel brightener is o-benzoyl sulfimide.

15. A composite electroplate in accordance with claim 10 wherein said over-layer plate is chromium.

16. A composite electroplate in accordance with claim

10 wherein said nickel plate directly overlies an electrodeposit consisting essentially of lustrous nickel.

17. A composite electroplate in accordance with claim 10 wherein said nickel plate directly overlies an electrodeposit consisting essentially of lustrous nickel and said over-layer plate is chromium. 5

18. A method in accordance with claim 2 wherein said overlayer is chromium.

19. A method in accordance with claim 1 wherein said material is dispersed in said bath during plating by air agitation. 10

20. A method in accordance with claim 2 wherein said material is dispersed in said bath during plating by air agitation.

21. A method in accordance with claim 1 wherein said overlayer is chromium. 15

22. A method in accordance with claim 1 wherein there is present in said solution at least one compound selected from the group consisting of boric acid, formates and citrates. 20

942,729

970,755

1,163,911

2,637,686

2,658,839

2,756,489

2,767,464

2,849,353

2,992,171

2,999,798

3,061,525

17,313/28

513,963

References Cited in the file of this patent

UNITED STATES PATENTS

Kern	Dec. 7, 1909
Rosenburg	Sept. 20, 1910
Hall	Dec. 14, 1915
McKay	May 5, 1953
Talmey et al.	Nov. 10, 1953
Morris	July 31, 1956
Nack et al.	Oct. 23, 1956
Kardos	Aug. 26, 1958
MacLean et al.	July 11, 1961
Eitel	Sept. 12, 1961
Grazen	Oct. 30, 1962

FOREIGN PATENTS

Australia	June 21, 1929
Great Britain	Oct. 26, 1939