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ARTICLE COATED WITH A COELECTRODEPOSIT OF NICKEL AND PLASTIC PARTICLES, AN OVERLAYER THEREON, AND METHOD OF MAKING SAID ARTICLE

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This invention relates to the cathodic co-deposition of multitudinous fine particles of certain bath-insoluble organic resins dispersed as fine powders in aqueous nickel electroplating baths. It relates especially to the co-deposition of nickel, cobalt or iron or their binary or ternary alloys with fine powders of certain wettable organic resins that have pronounced electrostatic properties.

We have found that these fine powdered resins, to be particularly described below, when dispersed in aqueous acidic nickel electroplating baths such as the Watts nickel bath, co-deposit very readily with the nickel. The nickel plate obtained from such a bath has multitudinous particles of the resin uniformly distributed and imbedded therein.

These fine resin powders have been found to deposit uniformly on vertical surfaces as well as shelf areas. The nickel or nickel alloy plate obtained by the practise of the present invention is attractive and decorative and in addition, has enhanced corrosion resistance properties, especially when given a final thin chromium plate of about 0.005 to about 0.05 mil thickness, and even to about 0.1 mil thickness.

According to the present invention, the bath-insoluble organic resin powders are added to acidic nickel or nickel alloy plating baths and electrodeposition is carried out using agitation, preferably air agitation to disperse the particles in the plating baths. The resin powders usable in the plating baths of this invention include saran resins which are thermoplastic resins obtained by polymerizing vinylidene chloride, or co-polymerizing vinylidene chloride with up to about 30% of other unsaturates such as vinyl chloride, acrylonitrile, acrylic, maleic, fumaric or itaconic acid esters, dichlorovinylidene fluoride, etc.; polyolefins such as polyethylene and polypropylene; polyphenyleneoxide; polycarbonate; acrylonitrile-butadiene-styrene; acetal; polymers of vinyl chloride, vinyl resin powders; and the various nylons which are polyamides obtained by reaction of a diamine and a dicarboxylic acid or derivatives thereof, or self condensation of an amino acid or derivatives thereof. Examples are nylon 6 obtained from polycondensation of caprolactam (or amino caproic acid); nylon 7 a polymer of ethyl amino heptanoate; nylon 66 and 610 from hexamethylenediamine with adipic acid and sebacic acid respectively, etc.

The particle sizes of the powders that co-deposit from the nickel and nickel alloy plating baths range from about 2 to 3 mils down to submicroscopic particles. There were often coarser resin particles dispersed in the plating baths, but the coarser particles (much greater than about 2 mils) did not readily co-deposit on vertical surfaces, and moreover were not quite as easily kept uniformly suspended in the plating solution.

These organic plastic or resin powders, as already mentioned, co-deposited very readily on vertical surfaces as well as shelf areas from semi-bright and bright nickel electroplating baths. Uniform co-deposition starts with the finest powders even with very thin plate, such as the plate obtained in 1 to 3 minutes plating time at about 40 to 50 amps/sq. ft. With the bright nickel plating baths co-deposition of the unpigmented resin particles of sizes

of about 0.2 mil to 2 mils (5 micron to 50 micron size particles) cause sparkly bright nickel plate when the deposits were of a thickness greater than about 0.1 mil. This sparkly bright nickel plate with the resin particles densely and uniformly packed in the surface is of pleasing decorative appearance and makes possible enhanced corrosion resistance when decoratively chromium plated. In plating over these sparkly bright nickel plates with a thin plate of about 0.005 to 0.1 mil thickness of chromium, gold, brass, or rhodium, the pleasing decorative sparkly effect persists in the new top surface.

Resin particles containing dyes and pigments of various colors including black dyes and pigments in general plated out as readily as the colorless to white resin particles. In one case, a green colored saran powder (Saran 220, lot 21–93) did not plate out as readily on vertical surfaces as did the uncolored or unpigmented Saran F 120. This latter resin powder co-deposits extremely readily with dull Watts nickel plate or bright nickel plate on vertical surfaces; the co-deposition occurs at a very surprisingly fast rate and with surprisingly coarse particles. For example, using a commercial grade of Saran F 120 powder and after plating to a thickness of 0.1–0.4 mil, the surface of the nickel plate is densely and uniformly covered with imbedded resin particles of about 40 to 50 micron diameters almost all touching each other, i.e. separated by as little as the particle radii or diameters. This densely populated nickel surface with co-deposited resin particles persists with continued deposition to thicknesses of up to 2 mil or even greater thicknesses of plate.

The specific gravity of certain resin particles such as those of nylon is very close to that of the nickel baths of the usual concentrations. In such cases, a large portion of the powder may float on the surface of the bath, but with air agitation or other means of stirring of the bath to give comparable solution agitation, the powder will be dispersed in the bath and co-deposited uniformly with the nickel plate. There are certain advantages in using resin powders like nylon that have a specific gravity very close to that of the plating bath and tend to float. When the bath is left undisturbed with no agitation, the particles float to the surface and can be removed from the bath by simply scooping them off or by dam overflowing the top. This method is simpler than decanting the solution necessary when using heavy powders which settle when the bath is not agitated, and very much simpler than separating out plastic or resin powders which settle slowly.

The resin powders of the proper particle size may be prepared by any suitable method such as by grinding, precipitation, etc. If a grinding technique is used, it may be necessary to cool the resin to a low temperature to make it harder and more friable during the grinding. Often it is desirable to wash the resin with solvent to remove any oily films or mold release agents which would otherwise hamper the wetting and the co-deposition of the particles with the nickel plate. It is also frequently desirable to use surface-active agents in the bath to increase the wetting out of the resin particles to aid the dispersion and co-deposition.

With one embodiment of the invention, conductive metallic or semi-metallic particles coated with a film of resin or plastic are plated out of acidic nickel baths also containing cobalt and/or iron. Thus conducting or semiconducting fine powders of lead, tin, chromium, silver, graphite, molybdenum sulfide, etc. are placed in contact with a dissolved resin solvent solution whereby a film of the resin coats the conductive powder. The treated powder is allowed to dry and then dispersed in the plating bath. Smooth plates are obtained which without the resin film, would have been rough and irregular due to plated metal growth on the protruding conductive particles.

It is also possible to coat non-conducting particles with

he resin materials used in this invention and then co-leposit the particles from an acid nickel or nickel alloy ›ath. By this technique, a non-conducting powder that :o-deposits poorly can be co-deposited to a greater ex-ent than is otherwise possible. Examples of such non-:onductor particles that cannot be co-deposited in their ›rdinary form are fluorocarbons such as Kel-F and Teflon ›articles. If these particles are treated to remove the fluo-ine atoms from the surface, they can be coated with ilms of the resins used in this invention and then can be :o-deposited. One method to remove the surface luorine atoms is by treatment with sodium in liquid ammonia. These particles are then treated with a ›olvent solution of the resin such as Saran F 120 resin, dried and added to the nickel plating bath. In some cases, t is preferred to first treat the non-conducting particles with an epoxy resin film, then followed by a resin of this nvention. By this method, it is possible to co-deposit fluorocarbon particles that greatly enhance the lubrication properties of the plated surface. In this respect, co-deposited nylon particles also help greatly in lubrication and anti-seizing problems. Further methods of improving lubrication is obtained by co-depositing resin coated solid lubricant powders that are conductors or semi-conductors such as fine powders of lead, lead-tin, copper plus lead particles in a ratio around 50 or 60 to 40, graphite, and molybdenum sulfide. For other engineering applications, it is possible to coat highly magnetic powders, such as Alnico powder, with resin films and obtain smooth co-deposits with nickel and nickel alloys. In most of these engineering uses, the use of dull or semi-bright nickel plate is usually preferred.

Also examples of non-conducting particles that co-deposit very readily such as fine glass particles, fine glass beads, colored or uncolored, or fine diamonds or diamond dust may be coated with these resin films, especially Saran F 120, and co-deposited even more readily from a nickel bath. Co-deposition on a vertical surface of these non-resinous particles in greater percentage with the nickel and nickel alloy plate is obtained as compared to the case wherein these particles are not coated with the Saran F 120 resin films.

For the most corrosion resistant decorative plate, the semi-bright and bright nickel plating baths containing the dispersed organic resin powders can be used to plate on top of regular bright nickel, on top of bright nickel that overlies semi-bright nickel, or on top of semi-bright nickel plate itself. There is then obtained a composite, duplex, or multi-plex decorative plate of extremely good atmospheric corrosion resistance when a final thin layer of chromium is applied of a thickness of about 0.005 to about 0.1 mil. The thin final chromium plate is made very porous by plating over the nickel surface that has multitudinous embedded or partially embedded particles that are non-conducting or very poorly conducting

The range of concentration of the organic resin particles dispersed in the nickel and nickel alloy plating baths can vary from about 1 gram per liter up to about 300 and even 400 grams/liter. In general, the optimum concentrations of the substantially bath-insoluble organic resin powders to use in the acidic nickel plating baths or nickel alloy plating baths is from about 5 to about 250 grams/liter.

The acidic nickel plating baths may be the sulfate or the Watts type, high chloride, sulfamate, fluoborate or mixtures thereof. The preferred buffer to use in boric acid, although formates, acetates, citrates, etc. may be used as sole buffers or as mixed buffers. Preferably, the bath is operated at a pH range of from about 2 to 6, and at temperatures of from about 60 to 160° F.

It has been found that generally the co-deposition rate is the highest in a Watts bath. The presence of sequestering agents such as ethylene diamine tetra-acetic acid in concentrations up to about 30 g./l. also helps the co-deposition rate of the resin particles.

The following examples of nickel and nickel alloy electroplating baths are listed to show some preferred examples of baths with dispersed organic resin particles that can be readily co-deposited with nickel or nickel alloy plates.

Example I

$NiSO_4.6H_2O$	grams/liter	200–250
$NiCl_2.6H_2O$	do	50–75
H_3BO_3	do	40
Saran F–120 powder (5 micron to about 50 micron particle size)	grams/liter	3–100
p-Toluene sulfonamide	do	0–2
Benzene sulfonamide	do	0–2
o-Benzoyl sulfimide	do	0–2
Temperature, ° F.		120–160
pH		2.5–5.0
Air agitation, cathode current density of		40–50 amps/sq. ft.

With 10 and especially 50 g./l. concentration of the Saran F–120 powder dispersed in the bath, the surface of the nickel deposit vertically plated (run as dull nickel or bright nickel) at the end of plating to about 0.5 mil thickness is densely packed with saran particles of about 40 to 50 micron particle diameters about one diameter or less apart as well as an equally large proportion of agglomerated particles touching each other and consisting of about 3 to 10 particles per clump, and consisting of small particles as well as larger particles. Apparently the much larger particles over 50 microns do not readily plate out on vertical surfaces.

Sodium 2-ethyl hexyl sulfate in a concentration of 0.1 to about 0.5 gram/liter helps to wet and disperse the resin powders and aids co-deposition in the above bath and those following.

Example II

$NiSo_4.6H_2O$	grams/liter	200–250
$NiCl_2.6H_2O$	do	40–80
H_3BO_3	do	40
p-Toluene sulfonamide	do	0–2
Benzene sulfonamide	do	0–2
o-Benzoyl sulfimide	do	0–2
Polyvinylchloride (PVC) resin (Goodyear Pliovic M–90)	grams/liter	1–100
Temperature, ° F.		120–160
pH		2.5–5.0
Air agitation, cathode current density of		40–50 amps/sq. ft.

With average particle size of the polyvinylchloride resin of about 15 microns and 1 gram/liter concentration of the powder, the surface of the dull or bright nickel plates at the end of plating to about 0.5 mil thickness, there were particles uniformly distributed about 5 to 8 diameters apart with a great deal of very very fine particles intermingled with predominantly uniform larger particles. At concentrations of 20 grams/liter, the density of particles in the surface of 0.5 mil thick nickel plate was now increased and the particles were now separated by only 1 to 3 particle diameters. At 50 grams/liter concentration, the density of the particles in the surface was not appreciably greater than at 20 grams/liter. Instead of the sulfonamide brighteners in the above bath, allyl sulfonic acid, benzene sulfonic acid or naphthalene sulfonic acid brighteners may be used.

Example III

$NiSO_4.6H_2O$	grams/liter	50–250
$NiCl_2.6H_2O$	do	200–50
H_3BO_3	do	40
EDTA	do	0–30
Nylon fine powder	do	1–200
p-Toluene sulfonamide	do	0–2
Benzene sulfonamide	do	0–2
o-Benzoyl sulfimide	do	0–2

Allyl sulfonic acid	grams/liter	0–4
8-methoxy coumarin	do	0–0.5
Temperature, ° F.		120–160
pH		2.5–5.0

Air agitation, cathode current density of 40–50 amps/sq. ft.

At concentrations of nylon powder of about 10 to 50 grams per liter, very uniform co-deposition of the nylon powder with the bath operated as a dull nickel or bright nickel occurred on both vertical and shelf areas, just as with the resins in Examples I and II.

The sequestering agents such as EDTA (ethylene diamine tetra-acetic acid and its salts), modified EDTA or NTA (nitrilotriacetic acid or its salts) and other sequestering agents, are very important additions to the high chloride acidic nickel plating bath for the purpose of increasing the concentration of fine organic powder plated out or co-deposited with the nickel plate. This is true for both bright nickel plate as well as semi-bright and dull nickel plate. EDTA is about the most effective agent for this purpose and is usually used in concentrations of about 15 grams/liter. It is very effective in promoting co-deposition of not only the organic resin particles but also inorganic particles such as fine silica powder, zirconium silicate powder, aluminum silicate powder, etc. The acidic high chloride nickel baths are those containing nickel chloride in concentrations of about 100 to 300 grams/liter with no nickel sulfate up to about 200 or 300 grams/liter of nickel sulfate. In the Watts nickel baths (high nickel sulfate concentration and low nickel chloride), a maximum concentration of the powders (organic or inorganic) are co-deposited, but with the use of the EDTA and/or other sequestering agents it is possible to co-deposit powders in substantially as high concentrations in the plate as can be done in Watts baths. The EDTA also helps in this respect in sulfamate nickel plating baths.

In the foregoing examples of baths of this invention nickel plating solutions were used because it is most desirable from a decorative point of view to co-deposit these resin particles in nickel baths or nickel alloy baths (where nickel is the predominating metal). However, these resin powders can be co-deposited in cobalt plating baths as well as ferrous iron plating baths. In these latter baths, that is, acidic cobalt and iron baths, the main value of the co-deposition of the resin particles is for engineering uses already described.

As previously pointed out, one of the outstanding benefits of the present invention is the ease of separating the organic resin powders from the plating bath. The need for separation of the resin powder from the plating bath may arise if the bath requires an activated carbon treatment to remove soluble organic contamination, or if the bath becomes contaminated with semi-metallic or metallic particles such as anode sludge which requires separation from the plating solution by filtration.

It was interesting and surprising (because of the low wettability) that microfine polyethylene resin consisting of spherical particles of about 8 to 30 micron diameters (Microthene FN500 sp. gr. 0.92) co-deposited with dull and bright nickel plate. However these particles did not plate out as readily as saran particles (Saran F–120) or acrylonitrile-butadiene-styrene (ABS) co-polymer. In the case of the saran particles as high as 2.5 weight percent (the volume percent is of course greater) can be co-deposited with the nickel on vertical surfaces. The resin powders of low water wettability such as the polyethylene, and the ABS co-polymer are best co-deposited with the nickel plate by using a surface-active agent such as sodium n-octyl sulfate or sodium 2-ethyl hexyl sulfate in the nickel plating bath to help wet the resins. The above low foaming wetting agents are preferably used when air agitation is employed in the baths to keep the resin particles dispersed. When mechanical agitation is used, a more powerful wetting agent such as sodium lauryl sulfate can be employed, because in this case foaming conditions would not be as readily created. In the above previous examples of plating baths, the use of the wetting agents 2-ethyl hexyl sulfate at 0.1 to 1 gram/liter and/or n-octyl sulfate at 0.1 to 0.5 gram/liter is recommended.

While certain specific organic resin powders have been described for use in the acidic plating baths, it follows from our work that other similar organic resin powders made from similar or different starting materials would co-deposite with the nickel or nickel alloy plates. The important properties necessary for co-deposition of the fine resin particles with the nickel, cobalt or iron plate is that they must have a requisite wettability not less than that of polyethylene, and must have a strong tendency to hold an electrostatic charge (saran is eminent in this respect). Cellulosic or modified cellulosic powders do not fit in this category and also are very gelatinous and there is little if any tendency to co-deposit with the nickel plate. Also surface-unmodified Teflon particles do not fit this category, as they are completely unwettable by the nickel plating bath.

The use of brightening agents in the nickel baths is not confined to the ones listed in the above examples. That is, benzene sulfonamides, benzene sulfonimides, benzene sulfonic acids, naphthalene sulfonic acids and other organic sulfon- brightening agents can be used. These organic sulfon- compounds can be used alone in the nickel baths or in mixtures or conjointly with unsaturated organic compounds such as allyl sulfonic acid, propargyl sulfonic acid, coumarin, 8-methoxy coumarin, formaldehyde, chloral hydrate, bromal hydrate, etc. Also the highly unsaturated compounds can be used alone to give semi-bright instead of fully bright nickel plate. In the latter case for semi-bright nickel plate the chloride concentration should be kept at low values, from zero to about 45 grams/liter of nickel chloride.

We claim:

1. A method of electroplating which comprises co-electrodepositing organic resinous particles with nickel from an aqueous acidic nickel bath containing an electrolyte selected from the group consisting of nickel sulfate, nickel chloride, nickel sulfamate, nickel fluoborate, and mixtures thereof and containing from 1 to about 300 grams per liter of insoluble organic resin particles dispersed therein having an avergae diameter less than about 50 microns selected from the group of resins consisting of saran, nylon, polyolefins, polyphenyleneoxide, acrylonitrile-butadiene-styrene polymers, acetal polymers, polyvinylchloride polymers, and mixtures thereof.

2. The method of claim 1 wherein said organic resin is a saran resin.

3. The method of claim 1 wherein said organic resin is a nylon resin.

4. The method of claim 1 wherein said organic resin is an acrylonitrile-butadiene-styrene polymer.

5. The method of claim 1 wherein said organic resin is a polyvinylchloride.

6. The method of claim 1 wherein said organic resin particles are dispersed in said bath by air agitation.

7. A method of electroplating which comprises co-electrodepositing organic resinous particles with nickel from an aqueous acidic nickel bath containing an electrolyte selected from the group consisting of nickel sulfate, nickel chloride, nickel sulfamate, nickel fluoborate, and mixtures thereof and containing from 1 to about 300 grams per liter of insoluble organic resin particles dispersed therein having an average diameter less than about 50 microns selected from the group of resins consisting of saran, nylon, polyolefins, polyphenyleneoxide, acrylonitrile-butadiene-styrene polymers, acetal polymers, polyvinylchloride polymers, and mixtures thereof, and thereafter electrodepositing on said surface an over-layer of less than 0.1 mil thickness of a metal selected from the group consisting of chromium, gold, brass, and rhodium.

8. The method of claim 7 wherein said over-layer is chromium.

9. An electroplating bath comprising an aqueous acidic nickel solution containing an electrolyte selected from the group consisting of nickel sulfate, nickel chloride, nickel sulfamate, nickel fluoborate, and mixtures thereof and containing from 1 to about 300 grams per liter of insoluble organic resin particles dispersed therein having an average diameter less than about 50 microns selected from the group of resins consisting of saran, nylon, polyolefins, polyphenyleneoxide, acrylonitrile-butadiene-styrene polymers, acetal polymers, polyvinylchloride polymers, and mixtures thereof.

10. A bath in accordance with claim 9 additionally containing dissolved therein a brightening agent selected from the group consisting of organic sulfon- compounds and organic unsaturated compounds.

11. A bath in accordance with claim 9 additionally containing a wetting agent dissolved therein.

12. A bath in accordance with claim 9 wherein said organic resin is saran.

13. A bath in accordance with claim 9 wherein said organic resin is nylon.

14. A bath in accordance with claim 9 wherein said organic resin is an acrylonitrile-butadiene-styrene polymer.

15. A bath in accordance with claim 9 wherein said organic resin is polyvinylchloride polymer.

16. An article comprising a substrate and an electroplate thereon, said electroplate comprising a nickel plate with a metallic over-lay, said nickel plate having been electrodeposited from an aqueous acidic nickel plating bath having dispersed therein from 1 to about 300 grams per liter of at least one type of insoluble organic resin particles having an average diameter less than about 50 microns selected from the group of resins consisting of saran, nylon, polyolefins, polyphenyleneoxide, acrylonitrile-butadiene-styrene polymers, acetal polymers, polyvinylchloride polymers, and mixtures thereof, and an electrodeposited over-lay plate of less than about 0.1 mil of a metal selected from the group consisting of chromium, gold, brass, and rhodium.

17. An article in accordance with claim 16 wherein said resin is saran and said over-lay is chromium.

18. An article in accordance with claim 16 wherein said resin is nylon and said over-lay is chromium.

19. An article in accordance with claim 16 wherein said resin is an acrylonitrile-butadiene-styrene polymer and said over-lay is chromium.

20. An article in accordance with claim 16 wherein said resin is a polyvinylchloride polymer and said over-lay is chromium.

References Cited

UNITED STATES PATENTS

1,702,927	2/1929	Bezzenberger	204—181 X
2,691,814	10/1954	Tait	29—195 X
2,999,798	9/1961	Eitel et al.	204—34
3,061,525	10/1962	Grazen	204—9
3,152,971	10/1964	Tomaszewski et al.	204—41
3,152,972	10/1964	Brown et al.	204—41
3,152,973	10/1964	Tomaszewski et al.	204—41
3,268,423	8/1966	Tomaszewski et al.	204—40
3,268,424	8/1966	Brown et al.	204—41

FOREIGN PATENTS

620,811	7/1962	Belgium.

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