United States Patent [19]

Michael

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[54] **METHOD FOR OBTAINING NICKEL DEPOSITS WITH SATIN FINISH**

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[21] Appl. No.: **353,662**

Related U.S. Application Data

[60] Division of Ser. No. 158,636, June 30, 1971, abandoned, which is a continuation-in-part of Ser. No. 725,492, April 30, 1968, abandoned.

[30] **Foreign Application Priority Data**

May 16, 1967 Germany 62744

[52] **U.S. Cl.** **204/49**

[51] **Int. Cl.** **C23b 5/08,** C23b 5/46

[58] **Field of Search** 204/49, 112; 106/1

[56] **References Cited**

UNITED STATES PATENTS

2,782,155	2/1957	DuRose et al.	204/49
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FOREIGN PATENTS OR APPLICATIONS

1,562,616	4/1969	France	204/49

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Attorney, Agent, or Firm—Hammond & Littell

[57] **ABSTRACT**

Aqueous acid nickel electroplating baths containing a basic polishing agent and 5 to 100 mg/liter of a substituted or unsubstituted adduct of ethylene oxide and/or propylene oxide emulsified in the bath and operated at bath temperatures of 40° to 75° C to form satin-finish nickel deposits and to the improved method of forming nickel deposits having a satin finish and the product produced thereby.

5 Claims, No Drawings

METHOD FOR OBTAINING NICKEL DEPOSITS WITH SATIN FINISH

PRIOR APPLICATIONS

This application is a division of copending application Ser. No. 158,636 filed June 30, 1971 now abandoned, which in turn is a continuation-in-part of copending, commonly assigned U.S. Pat. applications Ser. No. 725,492, filed on Apr. 30, 1968 now abandoned.

STATE OF THE ART

The usual practice in the formation of electroplating deposits is to obtain a coating as even and as highly polished as possible. In many cases, however, it is desirable to form metal deposits having satin finish such as in the case of nickel coated metal pieces used in automobiles which should be glare-free. Other important uses of satin finish metal pieces are in precision tool industries such as cameras, calculating machines, typewriters, modern steel tube furniture, etc.

Up to now, satin polish metal coatings were produced in several different ways, all of which were very costly. In one method, the surface of the metal which is to be coated is blasted with sand jets to first roughen the metal which is then coated in an ordinary nickel polishing bath. In another method, a bright nickel coating is produced and then is tarnished by a mechanical treatment but this reduces the corrosion resistance by weakening of the nickel coating. Moreover, the mechanical treatment required in both methods is very costly. Methods are known by which satin finish nickel deposits can be directly deposited without pre- or post mechanical treatment. These latter methods use ordinary nickel electropolating baths which are admixed with larger amounts of powdery materials insoluble in the baths such as kaolin, talcum, calcium, oxalate, etc., having a particle size of 0.1 to 0.3 μ. The powders are kept suspended in the bath by heavy air blowing through the bath and the powders are deposited along with the nickel as the electrolytic separation of nickel occurs which gives the coating a certain roughness, thereby giving a satin effect. This method requires special equipment and cannot be effected in ordinary electrocoating installations which results in high costs.

OBJECTS OF THE INVENTION

It is an object of the invention to provide novel nickel electrocoating baths for nickel deposits having a satin finish.

It is another object of the invention to provide a novel method of forming nickel deposits having a satin finish without any costly mechanical treatment and without special apparatus.

These and other objects and advantages of the invention will become obvious from the following detailed description.

THE INVENTION

The novel nickel electroplating baths of the invention are comprised of acid aqueous bath containing a water soluble nickel salt, a primary polishing agent and 5 to 100 mg/liter of an adduct emulsified in the bath electrolyte at 40° to 75°C, said adduct being selected from the group consisting of substituted and unsubstituted ethylene oxide, propylene oxide and ethylene oxide-propylene oxide adducts.

Suitable alkylene oxide adducts for the nickel electrocoating baths of the invention are adducts of the formula

$$R_1 [X(R_2O)_m (R_3O)_n]p R_4 \quad (1)$$

wherein X is selected from the group consisting of oxygen, sulfur or —NH—, R_1 and R_4 are selected from the group consisting of hydrogen and an organic radical, R_2 and R_3 are selected from the group consisting of ethylene and propylene and m, n and p are whole numbers and said adducts form turbid solutions at 40° to 75°C. The said adducts may be polyethylene oxide, polypropylene oxide, mixed adducts of ethylene oxide and propylene oxide and addition products of ethylene oxide and/or propylene oxide with mono- or polyvalent, saturated or unsaturated, straight or branch chain, aliphatic, cyloaliphatic, aromatic or heterocyclic alcohols, mercaptans, aldehydes, ketones, acetals, amines, carboxylic acids, carboxylic acid amides and phenols.

A preferred group of adducts of formula I are those in which X is oxygen or —NH— and R_1 and R_4 are hydrogen or aliphatic, aromatic or aliphatic-aromatic hydrocarbons or an acyl radical of an organic carboxylic acid of one to 18 carbon atoms. The said adducts where R_1 is other than hydrogen are formed by the addition of 2 to 300 moles of ethylene oxide and/or propylene oxide with 1 mole of an alcohol such as aliphatic alochols of one to 22 carbon atoms such as methanol, butanol, 2-ethylbutanol, 2-ethylhexanol, allyl alcohol, oleyl alcohol, etc.; polyhydroxyl alcohol of two to 22 carbon atoms such as glycol, propanediol, hexanediol, glycerin, erythrite, pentaerythrite, trimethylolpropane, sorbitol, polyglycerin, etc.; cycloaliphatic alcohols such as cyclohexanol; aromatic alcohols such as benzyl alcohol, etc.; mono-and polyamines of one to 22 carbon atoms such as ethylamine, ethylenediamine, triethanolamine, aniline, cyclohexylamine, etc.; aldehydes of one to 22 carbon atoms such as acetaldehyde, myristinaldehyde, benzaldehyde, etc.; ketones of three to 22 carbon atoms such as acetone, methyl ethyl ketone, acetophenone etc.; mono- and polycarboxylic acids of one to 22 carbon atoms and dimers thereof such as acetic acid, butyric acid, benzoic acid, oxalic acid, adipic acid, phthalic acid, oleic acid, cyclohexanecarboxylic acid, etc.; and amides of said carboxylic acids such as acetamide, benzamide, etc.; phenols of six to 22 carbon atoms which may be substituted such as phenol, cresol, nonylphenol, naphthol, etc.

In order to make the turbidity point of said adducts fall within the desired temperature range or to decrease the solubility of the adducts in the acid electroplating baths, the terminal hydroxyl group may be replaced with an organic radical R_4 by different reactions such as reaction with epichlorohydrin or benzylchloride, esterification with an organic carboxylic acid or acid chloride or other desired method.

Examples of specific adducts useful in the nickel electroplating baths of the invention are polyethyleneoxide with a molecular weight of 30,000, a mixed ethylene oxidepropylene oxide in a 3:1 ratio and having a molecular weight of 10,000, an adduct of 30 moles of propylene oxide and 10 moles of ethylene oxide to 1 mole of propylene glycol, adduct of 30 moles of propylene oxide and 40 moles of ethylene oxide to

1 mole of propylene glycol, adduct of 30 moles of propylene oxide and 9 moles of ethylene oxide to one mole of trimethylolopropane, adduct of 20 moles of ethyleneoxide and 10 moles of propylene oxide to one mole of cetyl alcohol, adduct of 20 moles of ethylene oxide to 1 mole of cetyl alcohol whose terminal hydroxyl group is reacted with epichlorohydrin, adduct of 9 moles of ethylene oxide and 12 moles of propylene oxide to one mole of nonylphenol, adduct of 30 moles of ethylene oxide and 10 moles of propylene oxide to one mole of dimerized fatty acids of linseed oil, adduct of 48 moles of ethylene oxide and 44 moles of propylene oxide to one mole of ethylenediamine, adduct of 5 moles of ethylene oxide to one mole of technical oleyl alcohol whose terminal hydroxy group is acetylated, adduct of propylene oxide to polyglycerin in a ratio of 10 moles of propylene oxide per hydroxyl group, adduct of 10 moles of ethylene oxide and 16 moles of propylene oxide to one mole of hexane—1, 6—diol, adduct of 33 moles of propylene oxide to one mole of trimethylolpropane, adduct of 10 moles of ethylene oxide and 30 moles of propylene oxide to one mole of phenol, etc. The said compounds are merely examples of specific adducts useful for the preparation of nickel deposits with satin finish. Other adducts can be made by the generally known alkoxylation reaction.

The adducts when added to the acid nickel plating baths have to form fine emulsions at the operating temperatures of 40° to 75° C. Some adducts will form clear solutions at room temperature but form the fine emulsions at operating temperatures, said emulsions being seen as turbidity which disappears when the bath is cooled.

The fine emulsions of the adducts in the acid nickel electroplating bath are usually very stable but in some cases it is useful to add up to 2 gm/liter of an emulsion stabilizer. Examples of suitable emulsion stabilizers are low molecular weight wetting agents such as branch chained alkyl sufates or sulfonates, i.e., isohexyl sulfonate, isononyl sulfate, isohexyl sulfate, hexyl sulfate, tetraline sulfonate, isopropylbenzol sulfonate, etc. The amount of stabilizer used should not be higher or the fine emulsion will change into micelluar mixtures. Particularly useful are 0.5 to 1.0 gm/liter of the alkyl sulfates.

The acid nickel electroplating baths should contain 5 to 100 mg/liter, preferably 10 to 50 mg/liter, of the adduct and 220 to 380 gm/liter, of the water soluble nickel salt. The said baths are operated at 40° to 75° C over a current density range of 0.5 to 10 A/dm^2 with a pH of 3.0 to 5.1, preferably 4.0 to 4.8, with or without air circulation.

The acid nickel electroplating baths also contain 0.2 to 10 gm/liter of known primary polishing agents such as in U.S. Pat. Nos. 2,238,861 and 3,023,151. Examples of suitable polishing agents are *m*-benzol disulfonic acid, naphthaline trisulfonic acid, diaryldisulfimides, sulfonamides, N-sulfonyl-carboxylic acid amides, saccharin, etc.

The size of the emulsified droplets in the bath determine the roughness depth of the nickel deposits and thereby their surface finish. The smaller droplets produce a fine satin finish and larger droplets produce a coarser satin finish. The size of the emulsion droplets can be varied by changing the alkylene oxide adduct and by the use of the emulsion stabilizer whereby it is possible to obtain specific satin finishes by proper selection of the adduct after a few preliminary tests. Moreover, the roughness depth for a specific adduct will not change with its concentration in the bath and is independent of the thickness of the nickel deposit and the pH value of the bath.

As water soluble nickel salts may be used sulfate, nickel sulfonate alone or in mixture with nickel chloride.

The acid nickel electroplating baths of the invention give a roughness depth anywhere in the range from 0.1 to 6.0 μ to form nickel deposits having a fine to rough satin finish with excellent average thickness and dullness. The said satin finish is obtained without any intermediate treatment with good adhesion directly on known bases such as iron, brass, copper, nickel, synthetic material made conductive, etc. Moreover, other metals such as chromium, gold, silver and copper can be plated over the satin nickel deposit while retaining the satin finish as well as bright nickel deposits thereon.

The use of polyalkylene oxide adducts in nickel electroplating baths at concentrations greater than 200 mg/liter as a wetting agent is known but the said adducts are always selected so they are soluble in the baths at operating temperatures. The said adducts were added to the baths to prevent pit formation in the nickel deposits, particularly with pore forming polishing agents such as polysulfonic acids, alkyl sulfonic acids and other known polishing agents. From this teaching of the use of alkylene oxide adducts in nickel electroplating baths to aid the polishing of nickel deposits, it was unforseeable that the adducts of the baths of the present invention could produce nickel deposits with a determinable satin finish and controlled roughness depth.

The acid nickel electroplating baths of the invention have the advantage of producing even nickel deposits having a satin finish and a roughness depth with can be varied over wide limits to give the most suitable and useful satin finish. Moreover, the baths may be used in common electroplating apparatus without any special equipment and no pre- or post- treatment is required to obtain a satin effect. Moreover, the baths have the advantage that they are relatively insensitive to changes therein and do not effect the nickel deposit.

In the following examples there are described several preferred embodiments to illustrate the invention. However, it should be understood that the invention is not intended to be limited to the specific embodiments.

EXAMPLE I

A basic nickel electroplating which was used for each of the following examples consisted of an aqueous solution having a pH of 4.0 to 4.8 and containing 265 gm/liter of nickel sulfate, 53 gm/liter of crystallized nickel chloride and 33 gm/liter of boric acid. To this bath there was added 2.5 gm/liter of N-acetyl-o-toluolsulfonamide and 2.0 gm/liter of sodium salt of naphthalene trisulfonic acid as the primary polishing agent, 1.0 gm/liter of sodium isononyl sulfate as a stabilizer and 0.03 gm/liter of an ethylene oxide-propylene oxide adduct having a molecular weight of 10,000 and an ethylene oxide to propylene oxide ratio of 3:1. When operating the bath at a temperature of 40° to 65°C and at a current density of 1 to 10 A/dm^2, ductile nickel coatings free from pores and having a satin-like

finish were obtained. The roughness depth with a nickel deposit 6 μ deep was approximately 4 μ and did not change over the entire current density range of 1 to 10 A/dm^2 and did not vary with nickel deposits 6 to 60 μ thick. The bath could be operated with or without air.

EXAMPLE II

2.5 gm/liter of N-acetyl-o-toluolsulfonamide and 1.0 gm/liter of sodium salt of naphthalene trisulfonic acid as primary polishing agents and 0.03 gm/liter of the addition products of 30 moles of propylene oxide and 10 moles of ethylene oxide to 1 mole of propylene glycol were added to the basic nickel electroplating bath. Operation of the bath at temperatures of 50° to 65°C and at a current density range of 1 to 8 A/dm^2 produced pore-free, ductile nickel deposits having a fine satin finish. The average roughness depth on a 6 μ thick nickel coating was about 1 μ and did not change over the entire current density range. The bath could be operated with or without air.

EXAMPLE III

1.0 gm/liter of saccharin and 2.0 gm/liter of sodium salt of naphthalene trisulfonic acid as primary polishing agents, 0.4 gm/liter of sodium hexylsulfate as emulsion stabilizer and 0.06 gm/liter of the addition product of 30 moles of propylene oxide and 40 moles of ethylene oxide to 1 mole of propylene glycol were added to the basic nickel electroplating bath. Operation of this electroplating bath at 55° to 70°C and over a current density range of 1 to 10 A/dm^2 gave pore-free, ductile nickel deposits having a fine satin polish. The average roughness depth of a 12 μ thick nickel deposit was about 1.5 μ. The bath could be operated with or without air.

EXAMPLE IV

2.5 gm/liter of N-acetyl-o-toluolsulfonamide as primary polishing agent and 0.05 gm/liter of the addition product of 30 moles of propylene oxide and 9 moles of ethylene oxide to 1 mole of trimethylolpropane were added to the basic nickel electroplating bath. Operation of this bath at 55° to 60°C over a current density range of 1 to 8 A/dm^2 provided pore-free, ductile nickel deposits having a satin finish. The roughness depth was about 0.4 μ over a nickel coating thickness range of 6 to 60 μ. The bath had to be operated with air.

EXAMPLE V

2.5 gm/liter of N-acetyl-o-toluolsulfonamide as the primary polishing agent and 0.04 gm/liter of the addition product of 20 moles of ethylene oxide and 10 moles of propylene oxide to 1 mole of cetyl alcohol were added to the basic nickel electroplating bath. Operation of this bath at 50° to 65°C and over a current density range of 1.5 to 8 A/dm^2 provided pore-free, ductile nickel deposits having a satinlike finish. The average roughness depth was 0.8 μ over a coating thickness range of 6 to 48 μ. The bath was operated with air.

EXAMPLE VI

1.0 gm/liter of saccharin as the primary polishing agent, 1.0 gm/liter of sodium hexylsulfate as an emulsion stabilizer and 0.04 gm/liter of the addition product of 20 moles of ethylene oxide to 1 mole of cetyl alcohol followed by reaction with one mole of epichlorohydrin for reaction with the terminal hydroxyl group were added to the basic nickel electroplating bath. Operation of this bath at 50° to 65° C over a current density range of 2 to 8 A/dm^2 provided porefree, ductile nickel deposits having a satin-like finish and having an even roughness depth of about 1.5 μ at a minimum nickel coating thickness of 12 μ. The bath could be operated with or without air.

EXAMPLE VII

3.0 gm/liter of N-acetyl-o-toluolsulfonamide as primary polishing agent and 0.04 gm/liter of the addition product of 9 moles of ethylene oxide and 12 moles of propylene oxide to 1 mole of nonylphenol were added to the basic electroplating bath. Operation of this bath at 50° to 70° C over a current density range of 0.5 to 8 A/dm^2 provided pore-free, ductile nickel deposits having a satin finish. The roughness depth of 0.8 μ did not change over coating thicknesses of 6 to 60 μ. The bath had to be operated with air.

EXAMPLE VIII

2.5 gm/liter of N-acetyl-o-toluolsulfonamide and 5.0 gm/liter of sodium m-benzoldisulfonate as primary polishing agents, 1.0 gm/liter of sodium isononyl sulfate as emulsion stabilizer and 0.03 gm/liter of the addition product of 30 moles of ethylene oxide and 10 moles of propylene oxide to 1 mole of dimerized fatty acids derived from linseed oil were added to the basic electroplating bath. Operation of this bath at 45° to 65 ° C over a current density range of 1 to 8 A/dm^2 produced pore-free, ductile nickel deposits having a completely uniform satin finish. The average roughness depth was about 0.8 μ for a nickel coating 12 μ thick. The bath could be operated with or without air.

EXAMPLE IX

2.5 gm/liter of N-acetyl-o-toluolsulfonamide as primary polishing agent, 1.0 gm/liter of sodium isononyl sulfate as emulsion stabilizer and 0.03 gm/liter of the addition product of 48 moles of ethylene oxide and 44 moles of propylene oxide to 1 mole of ethylenediamine were added to the basic electroplating bath. Operation of this bath at 45° to 65° C over a current density range of 0.5 to 8 A/dm^2 provided pore-free, ductile, light colored, dull nickel deposits having an average roughness depth of about 2.5 μ.

EXAMPLE X

2.5 gm/liter of N-acetyl-o-toluolsulfonamide as primary polishing agent and 0.04 gm/liter of the addition product of 5 moles of ethylene oxide with one mole of technical grade oleyl alcohol whose terminal hydroxyl group has been blocked by acetylation were added to the basic electroplating bath. Operation of this bath at 45° to 65° C over a current density of 1 to 8 A/dm^2 with air provided pore-free, ductile, light colored, dull nickel deposits having a deposit 12 μ thick and a roughness depth of 1 μ.

EXAMPLE XI

1.0 gm/liter of saccharin as primary polishing agent and 0.05 gm/liter of the addition product of 10 moles of propylene oxide per mole of hydroxyls in a polyglycerin were added to the basic electroplating bath. Oper-

ation of this bath at 50° to 70° C over a current density range of 1 to 8 A/dm² produced pore-free, ductile, satin-finish nickel deposits having a minimum thickness of 6 μ and an average roughness depth of about 0.5 μ. Operation of the bath required air.

EXAMPLE XII

2.5 gm/liter of N-acetyl-o-toluolsulfonamide as the basic polishing agent, 0.03 gm/liter of polyethylene oxide having a molecular weight of 30,000 and 0.01 gm/liter of the addition product of 10 moles of ethylene oxide and 16 moles of propylene oxide to 1 mole of hexane-1,6-diol were added to the basic electroplating bath. Operation of the bath with air circulation at 50° to 65° C over a current density range of 2 to 8 A/dm² produced ductile, pore-free, dull nickel deposits. The average roughness depth was about 1.2 μ at a nickel thickness of 12 μ.

EXAMPLE XIII

3.0 gm/liter of N-acetyl-o-toluolsulfonamide and 1.0 gm/liter of sodium salt of naphthalene trisulonic acid as basic polishing agents, 0.5 gm/liter of sodium isononyl sulfate as an emulsion stabilizer and 0.05 gm/liter of the addition product of 33 moles of propylene oxide with 1 mole of trimethylolpropane were added to the basic electroplating bath. Operation of the bath with air circulation at 40° to 55°C over a current density range of 1 to 8 A/dm² produced ductile, pore-free nickel deposits having a satin finish. The average roughness depth was about 0.7 μ with a minimum nickel thickness of 6 μ.

EXAMPLE XIV

1.0 gm/liter of saccharin and 1.0 gm/liter of N-acetyl-o-toluolsulfonamide as basic polishing agents, 0.6 gm/liter of the addition product of 10 moles of ethylene oxide and 30 moles of propylene oxide to 1 mole of phenol were added to the basic electroplating bath. Operation of the bath at 45° to 65°C over a current density range of 1.5 to 8 A/dm² produced ductile, pore-free, light-dull nickel deposits having an even roughness. The average roughness depth was 1 μ for a nickel deposit 6 μ thick. The bath could be operated with or without air circulation.

Various modifications of the baths and method of the invention may be made without departing from the spirit or scope thereof and it is to be understood that the invention is to be limited only as defined in the appended claims.

We claim:

1. In a process of forming ductile, pore-free nickel deposits by passing an electric current at a current density of 0.5 to 10 A/dm² at an operating temperature of 40°–75°C through an acid aqueous electroplating bath containing a water-soluble nickel salt, a primary polishing agent and an adduct having the formula

$$R_1 [X(R_2O_m (R_3O)_n]p R_4$$

wherein *X* is selected from the group consisting of oxygen, sulfur and —NH—, R_2 and R_3 are selected from the group consisting of ethylene and propylene, *m*, *n* and *p* are whole numbers and R_1 and R_4 are selected from the group consisting of hydrogen and an organic radical, the improvement comprising a sufficient amount of adduct being present in the bath so that the adduct is emulsified in the bath at the operating temperature, said amount being 5 to 100 mg per liter of bath whereby a satin-finish nickel deposit is obtained.

2. The process of claim **1** wherein X is selected from the group consisting of oxygen and —NH and R_1 and R_4 are selected from the group consisting of hydrogen, acyl radical of an organic carboxylic acid of one to 18 carbon atoms and aliphatic, aromatic and aliphatic-aromatic hydrocarbons of one to 22 carbon atoms.

3. The process of claim **1** wherein the bath contains 10 to 50 mg per liter of the said adduct.

4. The process of claim **1** wherein a branched chain aklyl sulfate in a concentration of 0.5 to 1.0 gm/liter is present as a wetting agent.

5. The process of claim **1** wherein the bath also contains up to 2 gm per liter of a wetting agent.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,839,166 Dated October 1, 1974

Inventor(s) Gregor Michael

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, line 16, "$R_1[X(R_2O_m(R_3O)_n]_p R_4$"

should read -- $R_1[X(R_2O)_m(R_3O)_n]p\ R_4$ --.

Signed and Sealed this

twenty-ninth Day of June 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

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Commissioner of Patents and Trademarks