NICKEL ELECTROPLATING METHOD

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ABSTRACT
An improved method of forming nickel deposits having a satin finish, which satin finish is obtained by the presence of a fine emulsion of an alkylene oxide adduct in the bath electrolyte, which improvement comprises periodically cooling at least a portion of the bath electrolyte below the turbidity point to obtain a homogeneous solution and then warming the bath electrolyte to the operating temperature which reforms the emulsion of alkylene oxide adduct in the bath electrolyte.

3 Claims, No Drawings
NIQUEL ELECTROPLATING METHOD

PRIOR APPLICATIONS

This application is a division of copending U.S. 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. application Ser. No. 725,506 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 electroplating baths which are admixed with larger amounts of powdery materials insoluble in the baths such as kaolin, talcum, calcium oxide, 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 alone 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 electro-coating installations which results in high costs.

In U.S. Pat. application Ser. No. 353,662 filed concurrently herewith in the name of Gregor Michael and entitled Compositions and Method for Obtaining Nickel Deposits with Satin Finish, novel acid nickel electroplating baths are described by which nickel deposits having a satin finish are obtained. The said baths contain a primary polishing agent and 5 to 100 mg/liter of an adduct selected from the group consisting of substituted and unsubstituted polyethylene oxide, polypropylene oxide and polyethylene oxide-propylene oxide which forms a fine emulsion in the acid bath at 40° to 75°C and cooling at least a portion of the acid aqueous electroplating bath below the turbidity point to obtain a homogeneous solution and then reheating the cooled portion to the operating temperature to reform the adduct emulsion.

OBJECTS OF THE INVENTION

It is an object of the invention to provide a novel electroplating method for forming nickel deposits having a uniform satin finish over prolonged operating periods.

It is another object of the invention to provide a simple, economical method of controlling the degree of emulsion dispersion in an acid nickel electroplating bath.

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

THE INVENTION

The electroplating method of the invention comprises passing an electric current through an acid aqueous electroplating bath operating at 40° to 75°C containing a water soluble nickel salt, a primary polishing agent and 5 to 100 mg/liter of an adduct selected from the group consisting of substituted and unsubstituted polyethylene oxide, polypropylene oxide and polyethylene oxide-propylene oxide which forms a fine emulsion in the acid bath at 40° to 75°C and cooling at least a portion of the acid aqueous electroplating bath below the turbidity point to obtain a homogeneous solution and then reheating the cooled portion to the operating temperature to reform the adduct emulsion.

The cooling of the electroplating bath below the turbidity point of the alkylene oxide adduct in the bath causes the adduct to dissolve in the acid bath which becomes homogeneous and upon reheating the cooled bath to the operating temperature, the emulsion is reformed with the original degree of dispersion which insures nickel deposits with a uniform satin finish. The rate of increasing size of the adduct emulsified in the bath electrolyte depends upon several factors such as operating temperatures of the nickel bath, the specific adduct used, the presence or absence of a stabilizer and type of stabilizer used, etc. The relationship of these factors will alter the time the bath will first show signs of deviation in the nickel deposits having a satin finish and will determine the rhythm with which the coating and reheating cycle is to be effected.

The specific means of maintaining a uniform degree of emulsion of the adduct and thereby the uniformity of the satin finish can be varied. The electroplating bath may be operated until the first signs of deviation in the satin finish occur, the operation of the bath halted and the entire electroplating bath composition may be cooled below the turbidity point, then reheated up to the bath operation temperature and electroplating started again. This type of operation of the method of the invention is less desirable because of the prolonged shutdown of the bath while cooling and reheating the entire bath electrolyte.
A preferred method of the invention comprises periodically removing a portion of the electrolyte which is then cooled below the turbidity point, reheated to bath operation temperatures and then returned to the bath. The cooling and reheating procedure has to be performed more often, but the amount of electrolyte is smaller and there is no shutdown time for the operation. The amount of bath electrolyte to be withdrawn and the frequency thereof depend upon the factors which effect the droplet size of the emulsion. However, at hourly intervals, one-third to one-fourth, preferably one-eighth to one-twentieth, of the electrolyte volume is removed and treated. This has been found to be effective in guaranteeing a satin finish.

A particularly effective method of the invention comprises continuously removing a portion of the bath electrolyte, cooling and reheating the same and returning it to the electroplating bath. For conservation of heat, the bath electrolyte to be cooled is preferably passed through a heat exchanger in which the cooled electrolyte to be reheated is passed countercurrently therethrough so it is warmed by the electrolyte to be cooled. The bath electrolyte to be cooled is taken from the heat exchanger and passed to a cooling apparatus where it is cooled below the turbidity point. The cooled electrolyte is pumped through a filter trap to remove any solid impurities, passed countercurrently through the heat exchanger and then finally heated to the bath temperature by a flow heater, thereby reforming the emulsion of the desired degree of dispersion which is then added to the bath. The amount of electrolyte to be removed continuously is dependent on the same factors as above and have been found to be the same as intermittent withdrawal of the electrolyte, namely, one-third to one-fourth, preferably one-eighth to one-twentieth, of the total electrolyte volume per hour. Baths constantly operated by this technique for periods of weeks have consistently produced nickel deposits having a uniform satin finish.

Periodic addition of polyalkylene oxide adduct to the bath is only necessary to replace the minor amounts used up in the electroplating process. This has been found to be about 15 gm per 10,000 ampere hours. Preferably, additions of adduct are made every 8 to 12 hours of operation to replace the adduct consumed and insure uniform deposits.

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

$$R_4[X(R_2O)_m(R_3O)_n]_p R_4$$

wherein X is selected from the group consisting of oxygen, sulfur or —NH—, R_2 and R_3 are selected from the group consisting of hydrogen and an organic radical, R_4 and R_5 are selected from the group consisting of ethylen 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 oxides and addition products of ethylene oxide and/or propylene oxide with mono- or polyvalent, saturated or unsaturated, straight or branch chain, aliphatic, cycloaliphatic, aromatic or heterocyclic alcohols, mercaptans, aldehydes, ketones, acetics, 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_4, and R_5 are hydrocarbons 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_4 is other than hydrocarbon are formed by the addition of 2 to 300 moles of ethylene oxide and/or propylene oxide with one mole of an alcohol such as aliphatic alcohols 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, ethrith, pentaerythrite, trimethylolpropane, sorbitol, polyglycerin, etc.; cycloaliphatic alcohols such as cyclohexanol; aromatic alcohols such as benzy 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, myristinoldehyde, benzaldehyde, etc.; ketones of three to 22 carbon atoms such as acetone, methyl ethyl ketone, acetophene, 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 adduct 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 benzyl chloride, 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 oxide-propylene 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 trimethylolpropane, adduct of 20 moles of ethylene oxide 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 hydroxyl group is reacted and 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 trimeth-
ylolpropane, adduct of 10 moles of propylene 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 alkoxilation reaction.

The adducts when added to the acid nickel plating baths have to form free emulsions at the operating temperatures of 40° to 75°C. Some adducts will form clear solution 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 sulfates or sulfonates, i.e., isohexyl sulfonate, isononyl sulfate, isohexyl sulfate, hexyl sulfonate, tetraline sulfonate, isopropylbenzyl sulfonate, etc. The amount of stabilizer used should not be higher or the fine emulsion will change into micellar 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/dm² with a pH of 3.5 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, naphthalene trisulfonic acid, diaryldisulfimides, sulfonamides, N-sulfonyl-carboxylic acid amides, saccharin, etc.

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

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 1

The basic nickel electroplating bath used in the following examples had a bath volume of 30 liters and consisted of an acid aqueous solution containing 265 gm/liter of crystalline nickel sulfate, 53 gm/liter of crystalline nickel chloride and 33 gm/liter of boric acid.

2.5 gm/liter of N-acetyl-o-toluol sulfonamide and 1.0 gm/liter of sodium salt of naphthalene trisulfonic acid as primary polishing agents and 0.03 gm/liter of an adduct of first 30 moles of propylene oxide and then 10 moles of ethylene oxide to one mole propylene glycol having a turbidity point of 25°C in the bath were added to the basic electroplating bath. Operation of the said bath at 55°C over a current density range of 1 to 8 A/dm² produced pore-free, ductile nickel deposits having a fine satin finish. The roughness depth was about 1 μ at a nickel thickness of 6 μ. After an hour of operation, there were no discernible differences in the satin finish of the nickel deposits. Thereafter, an almost imperceptible roughening of the satin finish began and after 3 hours of operation the nickel deposit had a roughness depth of 2.5 μ and the nickel deposits were also brighter than the nickel deposits first produced.

The said operation was repeatedly using the method of the invention. 10 liters of the bath electrolyte (one-third of the bath volume) per hour were removed from the bath and led through a heat exchanger in which electrolyte cooled to 24°C flowed countercurrently, whereby the electrolyte temperature dropped from 55° to about 45°C. In a cooling apparatus, the temperature of the electrolyte was then cooled to 24°C, 1° below its turbidity point, so that a completely homogeneous electrolyte was obtained. Then, the cooled electrolyte was pumped through a customary filter trap to remove impurities and was then passed through the heat exchanger countercurrent to freshly removed bath electrolyte. The returning electrolyte was heated thereby to about 34°C and was then passed through a flow heater to obtain a 55°C temperature before being returned to the bath.

The said bath with the cooling, warming recirculation produced nickel deposits after 24 hours operation which were identical to nickel deposits produced after one hour operation which had an average roughness depth of 1 μ. No polyalkylene oxide adduct was added to the bath during the first 24 hours. By adding 0.6 gm of the polyalkylene oxide adduct to the electrolyte at each 24 hour interval, the bath was operated continuously without interruption for weeks without change in the nickel deposits.

EXAMPLE 2

2.5 gm/liter of N-acetyl-o-toluol sulfonamide as the primary polishing agent, 1.0 gm/liter of sodium isononyl sulfonate as emulsion stabilizer and 0.03 gm/liter of the adduct of first 44 moles of propylene oxide and then 48 moles of ethylene oxide with 1 mole of ethylenediamine were added to the basic nickel electroplating bath which had a bath volume of 40 liters and a turbidity point of 35°C.

Operation of the said bath at 55°C over a current density range of 0.5 to 8 A/dm² produced pore-free, light, dull, ductile nickel deposits having an average roughness depth of 2.5 μ. For the first 2.5 hours the nickel deposits did not show any variations but after 5 hours of operation, the nickel deposits had a roughness depth of 3.5 μ due to the formation of larger droplets in the emulsion and the nickel deposits became brighter as well as taking on a new appearance.

The operation was repeated with 5 liters of electrolyte (one-eighth of bath volume) per hour being cooled and heated as in Example 1, except that the electrolyte was only cooled to 34°C. After 24 hours of operation,
the nickel deposits had a roughness depth of 2.5 μ, the same as after the first 2 hours of operation. Addition of 0.7 gm of the polyalkylene oxide adduct at 24 hour intervals permitted continuous operation of the bath without change in the nickel deposits.

**EXAMPLE 3**

2.5 gm/liter of N-acetyl-o-toluol sulfonamide and 0.5 gm/liter of sodium salt of m-benzol disulfonic acid as primary polishing agents. 1.0 gm/liter of sodium isononyl sulfate as emulsion stabilizer and 0.03 gm/liter of the adduct of first 30 moles of ethylene oxide and then 10 moles of propylene oxide to one mole of dimerized fatty acids of linseed oil were added to the basic electroplating bath which had a bath volume of 100 liters and had a turbidity point of 27°C.

Operation of the bath at 50°C over a current density range of 1 to 5 A/dm² produced ductile, level, pore-free nickel deposits having a satin finish. The nickel layer was 12 μ thick and the average roughness depth was 0.8 μ. During the first 3 hours of operation, there was no visible variation in the nickel deposits and then a barely perceptible roughening of the satin finish and increase in brightness began until after 8 hours of operation the average roughness depth was 2 μ. The increased brightness completely changed the character of the satin finish.

The operation was repeated with 5 liters of electrolyte (one-twentieth of the bath volume) per hour being removed from the bath with cooling and heating as in Example 1. The electrolyte leaving the heat exchanger had a temperature of 40°C and was then cooled to 26°C to obtain a completely homogeneous solution. All nickel deposits produced during this operation were identical in appearance and had an average roughness depth of 0.8 μ. Addition at 24 hour intervals of 1.8 gm of the polyalkylene oxide adduct to the bath permitted continuous operation of the bath without change in the nickel deposits.

**EXAMPLE 4**

1.0 gm/liter of saccharin and 2.0 gm/liter of the sodium salt of naphthalene trisulfonic acid as primary polishing agents, 0.4 gm/liter of sodium hexyl sulfate as emulsion stabilizer and 0.06 gm/liter of the adduct of first 30 moles of propylene oxide and then 40 moles of propylene oxide to one mole of propylene glycol were added to the basic electroplating bath. The bath had a volume of 120 liters and a turbidity point of 34°C.

Operation of the bath at 55°C over a current density range of 1 to 10 A/dm² produced pore-free, ductile nickel deposits on iron, brass and copper having a satin finish. The nickel deposits were 12 μ thick and had an average roughness depth of about 1.5 μ. For the first 5 hours of operation, there was no perceptible difference in the nickel deposits but after this time barely perceptible roughness in the satin finish began to occur until after 10 hours of operation the roughness depth of the nickel deposits was about 3 μ and together with the increased brightness gave the nickel deposits a considerably different appearance.

The operation was repeated with 3 liters of electrolyte (one-fourtieth of bath volume) being removed per hour from the bath and cooled and warmed as in Example 1. The electrolyte leaving the heat exchanger had a temperature of 45°C and was then cooled to 33°C. The electrolyte was reheated to 55°C before introduction back into the bath. After 24 hours of operation, the nickel deposits had an average roughness depth of 1.5 μ and was identical to those produced at the beginning. The addition of 4.3 gm of the alkylene oxide adduct to the bath at 24 hour intervals allowed the bath to be operated for weeks without interruption.

**EXAMPLE 5**

The following comparative experiments were conducted in a Hull test cell with a basic acid aqueous nickel electroplating bath consisting of 265 gm. per liter of crystalline nickel sulfate, 53 gm per liter of crystalline nickel chloride, 33 gm per liter of boric acid, 2.5 gm per liter of N—acetyl-o-toluenesulfonamide and 1.0 gm per liter of sodium naphthalenetrisulfonate and having a pH of 4.0 to 4.8.

**TEST 1**

0.03 gm per liter of an adduct of 30 moles of propylene oxide and 10 moles of ethylene oxide to one mole of propylene glycol was added to the basic bath and electropolishing was effected on a polished brass plate at one ampere for 10 minutes at a bath temperature of 21°C—23°C which resulted in a nickel deposit over a wide current density range. A highly polished nickel deposit was obtained over almost the entire plate with a scorched occurring only at the low current density of 0.1 to 0.2 A/dm². The bath solution remained completely clear and the adduct was completely dissolved as the turbidity point was not reached at this temperature.

**TEST 2**

The procedure of Test 1 was repeated with 0.5 ampere for 20 minutes at a bath temperature of 21°C. A highly polished nickel deposit over the entire surface of the metal plate was obtained and the bath solution was again completely clear as the adduct was completely dissolved.

**TEST 3**

The procedure of Test 1 was repeated except the bath temperature was 55°C. A nickel deposit with a fine satin finish covered the entire plate and the bath solution was cloudy as the adduct was emulsified in the bath.

**TEST 4**

The procedure of Test 2 was repeated except the bath temperature was 55°C. A nickel deposit with a fine satin finish covered the entire plate and the bath solution was cloudy as the adduct was emulsified in the bath.

**TEST 5**

The procedure of Test 3 was repeated except the adduct was 0.03 gm per liter of the adduct of 16 moles of propylene oxide and 22 moles of ethylene oxide to 1 mole of propylene glycol. A highly polished nickel deposit was obtained in the medium to low current density range and a blackish precipitate was obtained in the highest current density range. The bath solution was completely clear as the adduct was completely dissolved at the operating temperature 40° to 75°C.

The foregoing tests clearly show that the alkylene oxide adducts have to be used at a concentration sufficient to form a finely divided emulsion in the bath electrolyte at the operating temperature of 40°—75°C. to obtain a nickel deposit with a satin finish rather than a highly polished nickel deposit.

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 an electroplating method for forming nickel deposits having a uniform satin finish in which electric current is passed through an acid aqueous nickel electroplating bath operating at 40° to 75°C in which the electrolyte contains a water soluble nickel salt, a primary polishing agent and 5 to 100 mg/liter of an adduct having the formula R₃[X-(R₂O)ₙ(R₃O)ₚ]R₄ wherein X is selected from the group consisting of oxygen, sulfur and —NH—R₃ and R₄ are selected from the group consisting of ethylene and propylene, m, n and p are whole numbers and R₁ and R₂ are selected from the group consisting of hydrogen and an organic radical which amount of adduct forms a fine emulsion in the acid bath at 40° to 75°C, the improvement which comprises continuously removing a portion of the electrolyte from the bath, passing the electrolyte through a heat exchanger in which cooled electrolyte is passed countercurrently and then through a cooling apparatus to cool the electrolyte below the turbidity point, passing the cooled electrolyte countercurrently through the heat exchanger and reheating the said electrolyte to the bath temperature and adding the electrolyte back to the bath.

2. The method of claim 1 wherein one-third to one-fortieth of the total volume of the electrolyte is cooled and reheated each hour of operation.

3. The method of claim 1 wherein the amount of electrolyte removed per hour is one-eighth to one-twentieth of the total volume.

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