United States Patent

Merker et al.

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[54] METHOD FOR ELECTROPLATING NICKEL

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

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

[58] **Field of Search** 204/49

[56] **References Cited**

UNITED STATES PATENTS

3,152,975	10/1964	Kardos et al.	204/49
3,220,940	11/1965	Brown et al.	204/49
3,386,897	6/1968	Ostrow et al.	204/49
3,399,123	8/1968	Passal	204/49

FOREIGN PATENTS OR APPLICATIONS

1,164,192	2/1964	Germany	204/49

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[57] **ABSTRACT**

Method for electroplating nickel to obtain a bright deposit by adding to a conventional nickel acidic bath solution effective amounts of a brightening agent having the general formula

$$RSO_2NY(CH_2CH_2O)_nZ$$

where R is a phenyl, alkyl or alkenyl radical with one to 14 carbon atoms, Y is hydrogen or an alkyl radical with one to six carbon atoms, n is a numeral from one to six, and Z is a metal imparting water solubility to the brightening agent.

5 Claims, No Drawings

METHOD FOR ELECTROPLATING NICKEL

FIELD OF THE INVENTION

The present invention is directed to a process of plating nickel from acidic bath solutions, and more particularly, to the production of bright nickel platings having improved characteristics.

THE PRIOR ART

The use of sulfonamides and sulfonimides as primary or carrier type brighteners has long been known in the art. These brighteners have also proven capable of promoting the production of low stress ductile deposits when present in a sufficiently high concentration. They have been employed alone or in conjunction with secondary addition agents which increased the brightness and, in many cases, the leveling characteristics of the nickel bath.

One known brightener has been saccharin, the sodium salt of benzene sulfonimide or NaO-sulfobenzoic imide. Because of its solubility in water, it not only offered a means of securing a high concentration thereof in the plating bath, but also a convenient method of making additions to the plating bath. Since saccharin has a high degree of solubility, it became possible to make a concentrated solution and conveniently add it to the bath. When it is used in a Watts bath with acetylenic compounds (such as 2-butyne, 1-4 diol), it is also an effective haze remover. On the other hand, other sulfonamides, such as benzene sulfonamide tend to produce hazy or cloudy deposits with the acetylenic compounds. These hazy deposits may be corrected only by the addition of a sulfonic acid, such as benzene sulfonic acid.

Saccharin has the most undesirable characteristic of producing poor, dark, low current density deposits when the bath is contaminated with zinc or copper. Such contamination is quite common when plating zinc die castings commercially.

Benzene sulfonamide or its sodium salt when used in nickel plating baths acts similarly to saccharin as a stress reducer. However, it has limited solubility making it difficult to dissolve in the bath. Also, where relatively high concentration of the sufonamide are required to carrying the secondary brighteners or for greater stress reduction, the limited solubility thereof limits its use. When used in conjunction with acetylenic secondary brighteners, it has a tendency to produce hazy deposits and it requires the addition of an aryl sulfonic acid such as benzene sodium sulfonate.

The halogen substituted derivatives of the sulfonamides and imides produce better leveled deposits than the unsubstituted compounds; however, they have poorer solubility. As a result, it becomes impossible to secure the optimum concentration thereof in the plating bath.

The sulfonamides and sulfonimides have decreased solubility at low pH values and, where low stressed deposits are required in nickel plating baths at pH of 1–2, it becomes impossible to secure sufficient beneficial concentration in solution.

One method of solubilizing the brightener employed in the bath solution is described in U.S. Pat. No. 3,386,897 to Ostrow. According to this patentee, the solubilization is obtained by introducing in the conventional acidic nickel plating bath an organic compound which contains both at least a sulfonamide group and at least a sulfonic acid group.

BRIEF SUMMARY OF THE INVENTION

The present invention is intended to overcome the defects and disadvantages inherent in many prior paths of the character described above and to obtain results equal, if not superior, to those of Ostrow's, by providing a nickel plating process which will result in soft, ductile and adherent deposits on the basis metal, and haze-free over a broad current density range, particularly when acetylenic compounds are used as secondary brighteners.

It is further among the objects of the invention to provide a bath in which the additives have high solubility, give good tolerance to impurities in the bath, such as copper, zinc, lead, etc., and which promote leveling in the deposit.

It is still further among the objects of the invention to provide a bath which contains addition agents which retain their solubilities at low pH values of the order of 1–2.

DESCRIPTION OF THE INVENTION

In practicing the invention, there is introduced into the usual acid nickel plating bath, an organic primary brightener which contains both at least one sulfonamide group and at least one ethoxy group. The present brighteners are applicable to baths in which practically all of the known secondary brighteners are incorporated. These brighteners may be designated as ethoxylated benzene sulfonomides. They have unusually high water solubility and they impart exceptional zinc and copper tolerance to the nickel bath. They impart bright haze-free deposits when used with secondary acetylenic addition agents.

This class of brightening agent may be used alone where maximum luster and leveling are not required. They may be used in conjunction with other known primary or secondary brighteners such as acetylenic alcohols, acetylenic glycols and polyglycols, acetylenic amines and polyamines, quaternary pyridinium and quinoline compounds, allyl alcohols and amines, vinyl pyridine, triphenyl methane derivatives, aromatic sulfonic (mono and poly) acid salts.

The new compounds may be designated by the following general formula:

$$R\text{-}SO_2NY(CH_2CH_2O)_nZ$$

wherein R is a radical taken from the class consisting of phenyl, naphthyl, alkyl, alkenyl and alkynyl, having from one to 14 carbon atoms; n is a numeral from one to six; Z is a radical taken from the class consisting of hydrogen and a metal imparting water solubility to said agent; and Y is a radical taken from the class consisting of hydrogen and alkyl having one-six carbon atoms. These radicals may have substituents which do not adversely affect the desired properties of the compounds.

Among the advantages of the additives is the high solubility even at low pH values, being about 200 to 500 grams per liter compared to 1 to 3 grams per liter of the benzene sulfonamide or 200 to 400 grams of the sulfonamic-sulfonic acid mixture. This allows the production, shipment and storage of concentrated solutions with substantial savings. It permits the introduction into the bath of say 0.05 gram per liter to saturation, preferably up to 50 grams per liter. Even when chlorinated to obtain improved leveling, the solubilities of the present additives are in the neighborhood of 100 grams per liter. It is advantageous to add these brighteners to the bath in the form of concentrated solutions, both for accuracy and convenience. The alkene and alkyne derivatives give improved results. The brighteners are suitable for use in various acid nickel plating baths, including those containing sulfamates. Freedom from haze is obtained.

R may also be alkyl, alkene, and alkyne radicals having substituents thereon which do not adversely affect their properties. Aromatic radicals may be polynuclear, and have such substituents thereon such as alkyl, sulfo, halo, nitrilo, sulfoalkyl, amino and halo alkyl groups. Z may be, for instance, sodium, potassium, hydrogen, magnesium, cobalt, nickel and others.

Typical brightening agents suitable for the process of the invention are: benzene-sulfon-mono-ethoxy-amide, p-toluene benzene-sulfon-di-ethoxy-amide, p-bromo-benzene-sulfon-tri-ethoxy-amide, benzene meta-di-sulfon-tri-ethoxy-amide, alpha-naphthalene sulfon-di-ethoxy-amide, beta-naphthalene sulfon-di-ethoxy-amide, allyl-sulfon-di-ethoxy-amide, o-benzoic-sulfon-di-ethoxy-amide, p-toluene sulfon-mono-chloro-di-ethoxy-amide.

All of these compounds may be employed in the Watts bath solution given hereinafter, in various quantities ranging up to saturation, and in every instant a bright deposit may be obtained.

DETAILED EXAMPLES OF THE INVENTION

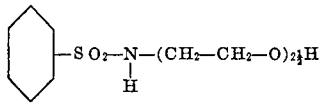
In the following specific examples, the Watts bath utilized has the following composition (in grams/liter):

Nickel sulfate	300
Nickel chloride	45
Boric acid	45
Na lauryl sulfate	0.25
Water to make 1 liter	

The pH is 3.0 to 5.0, temperature about 140° F, and the bath is agitated. Plating is conducted for the desired length of time in a Hull cell at a total current of 2 amperes for a period of 10 minutes.

EXAMPLE 1

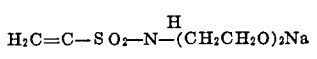
To the above Watts bath there is added 10.0 grams of



per liter of bath solution. The resulting plate was bright at current densities of from 0 to 50 amperes per square foot.

EXAMPLE 2

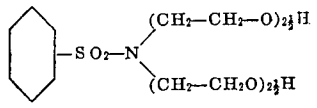
There is introduced into an all-chloride acid nickel plating bath 6.0 grams of



per liter of bath solution. A bright deposit was obtained on a steel panel plated in a Hull cell for 10 minutes at a current density of 2 amps/sq. foot.

EXAMPLE 3

Into the Watts bath there is introduced 18.0 grams of



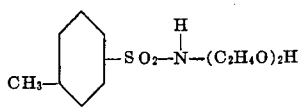
per liter of bath solution. A levelled and bright deposit was obtained over a steel panel in 5 minutes and at a current density of 1 amp/ft^2.

EXAMPLE 4

To the bath composition of example 1 were added 2 millimoles of ethoxylated methyl butynol. A fully bright deposit was obtained over the entire current density range from 1 to 80 amps/ft^2.

EXAMPLE 5

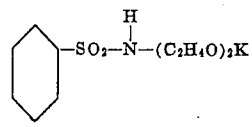
To the Watts bath of example 1 were added 7.0 grams of



per liter of bath solution. A levelled and bright deposit was obtained over a steel panel in 7.5 minutes and at a current density of 2 amps/sq. ft.

EXAMPLE 6

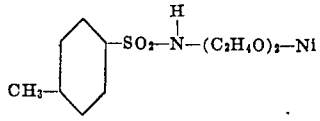
To the Watts bath of example 1 were added per liter of bath solution, 5.0 grams of



0.08 grams of butyndiol and 0.20 grams of sodium lauryl sulfate. A levelled and bright deposit was obtained over a steel panel at a current density of 2 amperes/sq. ft. in 10 minutes of plating operation in a Hull cell.

EXAMPLE 7

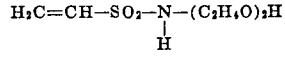
To the Watts bath of example 1 were added, per liter of bath solution 4.0 grams of



and 2.0 grams of benzene sulfonic acid. A bright deposit was obtained on a steel panel in a Hull cell in 5 minutes at a current density of 1 amp/sq. ft.

EXAMPLE 8

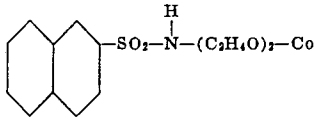
To an all chloride acid nickel bath were added, per liter of bath solution, 6.0 grams of



and 0.06 grams of propargyl amine. A fully bright and levelled deposit was obtained from a Hull cell on a steel panel in 10 minutes plating time at a current density of 2 amps/sq. ft.

EXAMPLE 9

To the Watts bath of example 1 were added, per liter of bath solution, 7.0 grams of



and 0.1 grams of butenediol. A bright deposit was obtained on a steel panel in a Hull cell in 10 minutes plating time at 2 amps/sq. ft.

What is claimed is:

1. A method of electroplating nickel to produce a bright deposit on a base metal which comprises providing an aqueous acid nickel bath having nickel ions therein introducing into said bath an effective amount of brightening agent having the general formula

$$RSO_2NY(CH_2CH_2O)_nZ$$

wherein R is a radical taken from the class consisting of phenyl, alkyl, and alkenyl, having from one to six carbon atoms; Y is a radical taken from the class consisting of hydrogen and alkyl from one to six carbon atoms; n is a numeral from one to six; and Z is a metal imparting water solubility to said agent; and passing an electric current through said bath to deposit a bright nickel low stress coating on said basis metal.

2. The method according to claim 1 wherein Y is hydrogen.

3. The method according to claim 1 wherein Z is an alkali metal.

4. The method according to claim 1 wherein the concentration of said agent is from about 0.05 gram per liter of bath solution to saturation.

5. The method according to claim 1 wherein the concentration of said agent is from about 0.05 to 50 grams per liter of bath solution.

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