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ELECTROPLATING BRIGHT NICKEL

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23 Claims. (Cl. 204—49)

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

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 stressed 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 of the most favored carrier brighteners 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 concentrations of the sufonamide are required for 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 concentrations in solution.

The present invention is intended and adapted to overcome the defects and disadvantages inherent in prior baths of the character described above, it being among the objects of the invention to provide a nickel plating bath and a process of plating which will result in soft, ductile and adherent deposits on the basis metal.

It is also among the objects of the invention to obtain bright haze-free deposits 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.

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 sulfonic acid group. By the introduction of such substances, the defects of prior additives have been overcome. The present brighteners are applicable to baths in which practically all of the known secondary brighteners are incorporated. These brighteners may be designated as sulfonic acid and sulfonic acid salts of sulfonamides. 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.

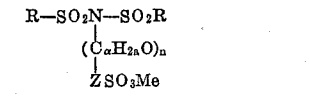
This class of brightening agent may be used alone where maximum luster and leveling are not required. They may be used in conjunction with other known primary or secondary brighteners such as acetylenic alcohols, acetylenic glycols and polyglycols, acetylenic amines and polyamines, quaternary pyridinium 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 formulas:

$$R—SO_2NY(C_aH_{2a}O)_n—Z—SO_3Me;$$

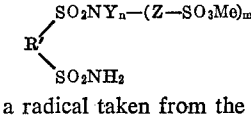
$$R—SO_2N[(C_aH_{2a}O)_n—Z—SO_3Me]_2$$

and



wherein R is a radical taken from the class consisting of phenyl, naphthyl, alkyl, alkenyl and alkynyl, having from 1 to 14 carbon atoms; n is a numeral from about 0 to 20, preferably from 0 to 6; Z is a radical taken from the class consisting of straight and branched chain hydrocarbons having 1–12 carbon atoms, phenyl and naphthyl; Me is a metal imparting water solubility to said agent; Y is a radical taken from the class consisting of hydrogen and alkyl having 1–6 carbon atoms; and a is a numeral from 1 to 3. These radicals may have substituents which do not adversely affect the desired properties of the compounds.

A similar group of closely related compounds have the following general formula:



wherein R′ is a radical taken from the class consisting of phenyl and naphthyl; Y is a radical taken from the class consisting of hydrogen and alkyl having 1–6 carbon atoms; n is a numeral from 0 to 1; m is a numeral from 1 to 2; m is 1 when n is 1, and m is 2 when n is zero. At least one hydrogen may be substituted by $Y_n—(ZSO_3—Me)_m$.

Among the advantages of the additives is the high solubility even at low pH values, being about 200 to 400 grams per liter compared to 1 to 3 grams per liter of the benzene sulfonamide. This allows the production, shipment and storage of concentrated solutions with substantial savings. It permits the introduction into the bath of say .05 gram per liter to saturation, preferably up to 50 grams per liter, which was impossible previously. 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 and 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. Me may be, for instance, sodium, potassium, hydrogen, magnesium, cobalt, nickel and others.

In the following specific examples, the bath preferably is of the following composition:

	G./l.
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 7.5 g./l. of ϕ—$SO_2N(C_3H_6$—$SO_3Na)_2$. The resulting plate was bright.

Example 2

Into the Watts bath there is introduced 5.0 g./l. of H_2C=CH—$SO_2N(C_3H_6SO_3Na)_2$ and electrolysis is conducted as usual. The plating is semi-bright to full bright and the deposit is well leveled.

Example 3

Excellent results are obtained by the addition of 8.0 g./l. of Cl_3—C—$SO_2N(CH_2$—CH_2—$SO_3Na)_2$ to the Watts bath.

Example 4

Into the Watts bath there is introduced the following composition:

	G./l.
ϕ—SO_2N—$(CH_2$—CH_2—CH_2—$SO_3Na)_2$	7.5
Allyl sulfonic acid sodium	0.5
Ethyl qinolinium iodide	0.02

The plating is bright and leveled.

Example 5

There is introduced into an all-chloride acid nickel plating bath 8.0 g./l. of H_2C=CH—$SO_2N(C_3H_6SO_3Na)_2$ which gives a bright deposit.

Example 6

Into a nickel sulfamate bath of the following composition:

	G./l.
Nickel (metal) as sulfamate	90.0
Nickel chloride	35.0
Boric acid	45.0

the following additives are introduced:

	G./l.
H_2C=CH—SO_2NH—CH_2—CH_2—SO_3K	0.5
Benzene sulfonic acid	4.0
Dipropargyl ethylene diamine	0.07

The pH is 3 to 4. Electrodeposition in a Hull cell with agitation is conducted for 10 minutes at 120°–130° F. with 2 amperes. The deposit is bright and level.

Example 7

Into the Watts bath there is introduced 15.0 g./l. of ϕ—SO_2NH—C_2H_4—SO_3Na, which gives a bright deposit.

By the addition of 0.005 g./l. of triaminotriphenyl methane the brightness of the deposit is enhanced.

Example 8

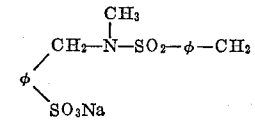
The following composition in the Watts bath also gives the desired properties to the plating:

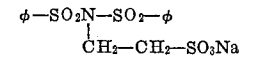
	G./l.
Cl—ϕ—$SO_2NH(O$—CH_2—$CH_2)_5$—C_2H_4—SO_3Na	4.0
$\phi SO_2NSO_2\phi$ $C_3H_6SO_3Na$	20

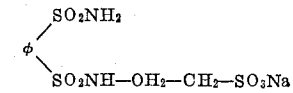
Many more additives of the type set forth herein and some of such compounds are listed below:

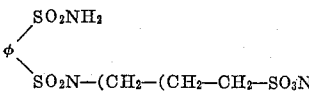
C_2H_5—SO_2NH—C_2H_4—SO_3Na

$C_2H_5SO_2N(C_2H_4SO_3Na)_2$









ϕ—$(SO_2N)_2$—$(CH_2$—CH_2—$SO_3Na)_4$

ϕ—SO_2NH—$(C_2H_4$—$O)_nC_3H_6$—SO_3Na

and

ϕ—$SO_2N[(C_aH_{2a}O)_n$—Z—$SO_3Me]_2$

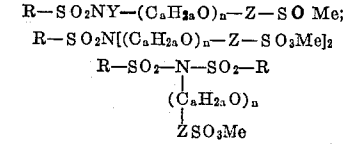
in which n may be up to 30. However, the lower ethoxylated sulfonamides having about 2 to 6 ethylene oxide groups are preferred. They impart added lustre to the deposit and they assist in the leveling.

What is claimed is:

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

R—SO_2NY—$(C_aH_{2a}O)_n$—Z—SO_3Me

R—$SO_2N[(C_aH_{2a}O)_n$—Z—$SO_3Me]_2$



wherein R is a radical taken from the class consisting of phenyl, alkyl, and alkenyl, having from 1 to 6 carbon atoms; Y is hydrogen; a is a numeral from 1 to 3; n is a numeral from 0 to 20; Z is a radical taken from the class consisting of straight chain hydrocarbons having 1–3 carbon atoms; and Me 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. A method according to claim 1 characterized in that n is a numeral from 0 to 6.

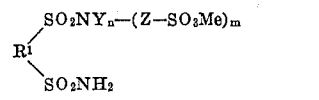
3. A method according to claim 1 characterized in that Me is an alkali metal.

4. A method according to claim 1 characterized in that the concentration of said agent is from about .05 gram per liter to saturation.

5. A method according to claim 1 characterized in that the concentration of said agent is from about .05 gram to 50 grams per liter.

6. A method according to claim 1 characterized in that said agent is halogenated.

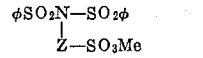
7. A method of electroplating nickel to produce a bright deposit on a basis metal which comprises providing an aqueous acid nickel bath having nickel ions therein, introducing into said bath an effective amount of a brightening agent taken from the class consisting of



wherein R' is phenyl; Y is hydrogen; Z is a radical taken from the class consisting of straight chain hydrocarbons having 1–3 carbon atoms, Me is a metal imparting water solubility to said agent; n is a numeral from 0 to 1; m is a numeral from 1 to 2; m is 1 when n is 1, and m is 2 when n is zero; and passing an electric current through said bath to deposit a bright nickel coating on said basis metal.

8. A method according to claim 7 characterized in that at least one H is substituted by $Y_n—(Z—SO_3Me)_m$.

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



wherein Z is a radical taken from the class consisting of straight chain hydrocarbons having 1–3 carbon atoms, and Me is a metal imparting water solubility to said brightener and passing an electric current through said bath to deposit a bright nickel coating on said basis metal.

10. A method of electroplating bright nickel which comprises introducing into an aqueous acid nickel bath having nickel ions therein an effective amount of a brightener having the following formula:

$$\phi SO_2N(C_3H_6—SO_3Na)_2$$

and electroplating said nickel from said bath.

11. A method of electroplating bright nickel which comprises introducing into an aqueous acid nickel bath having nickel ions therein an effective amount of a brightener having the following formula:

$$\phi SO_2NH(C_3H_6—SO_3Na)$$

and electroplating said nickel from said bath.

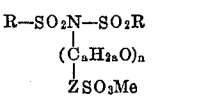
12. A method according to claim 1 characterized in that a sulfonic acid radical is attached to the aromatic ring.

13. A bath for electroplating nickel to produce a bright deposit comprising an aqueous acid nickel bath having nickel ions therein and an effective amount of a brightening agent taken from the class consisting of

$$R—SO_2NH—(C_aH_{2a}O)_n—Z—SO_3Me$$

$$R—SO_2N[(C_aH_{2a}O)_n—Z—SO_3Me]_2$$

and



wherein R is a radical taken from the class consisting of phenyl, alkyl and alkenyl having from 1–6 carbon atoms; n is a numeral from 0 to 20; a is a numeral from 1 to 3; Z is a radical taken from the class consisting of straight chain hydrocarbons having 1–3 carbon atoms; and Me is a metal imparting water solubility to said agent.

14. A bath according to claim 13 characterized in that n is a numeral from 0 to 6.

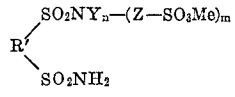
15. A bath according to claim 13 characterized in that Me is an alkali metal.

16. A bath according to claim 13 characterized in that the concentration of said agent is from about .05 gram per liter to saturation.

17. A bath according to claim 13 characterized in that the concentration of said agent is from about .05 gram to 50 grams per liter.

18. A bath according to claim 13 characterized in that said agent is halogenated.

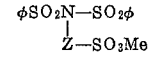
19. An aqueous acid nickel bath having nickel ions therein for electroplating nickel to produce a bright deposit comprising a sufficient amount to impart brightness to a deposit of



wherein R' is phenyl; Y is hydrogen; Z is a radical taken from the class consisting of straight chain hydrocarbons having 1–3 carbon atoms; Me is a metal imparting water-solubility to said agent; n is a numeral from 0 to 1; m is a numeral from 1 to 2; m is 1 when n is 1, and m is 2 when n is zero.

20. A bath according to claim 19 characterized in that H is substituted by $Y_n—(Z—SO_2Me)_m$.

21. An aqueous acid nickel bath having nickel ions therein for electroplating nickel and having therein an effective amount of a brightener, sufficient to produce a bright nickel deposit, of the following formula:



wherein Z is a radical taken from the class consisting of straight chain hydrocarbons having 1–3 carbon atoms and Me is a metal imparting water solubility to said brightener.

22. An aqueous acid nickel bath having nickel ions therein for electroplating nickel and having therein an effective amount of a brightener, sufficient to produce a bright nickel deposit of the following formula:

$$\phi SO_2N(C_3H_6—SO_3Na)_2$$

23. An aqueous acid nickel bath having nickel ions therein for electroplating nickel and having therein an effective amount of a brightener, sufficient to produce a bright nickel deposit, of the following formula:

$$\phi SO_2NH(C_3H_6—SO_3Na)$$

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