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ELECTRODEPOSITION OF NICKEL

Reuven Merker, Hempstead, and Herman P. Soguero, North Wantagh, N.Y., and Salvatore Lucca, Secaucus, N.J., assignors to The Metalux Corporation, Little Ferry, N.J., a corporation of New Jersey

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ABSTRACT OF THE DISCLOSURE

More brilliant and ductile nickel electrodeposits are obtained by incorporating into a conventional and known solution bath an additive having the formula

$$R_1R_2NSO_2NR_3R_4$$

in which the R radicals are selected from the group consisting of hydrogen, unsaturated alkyls with 2 to 6 carbon atoms, aryls, aralkyls, alkaryls, R—SO_3 radicals where R has 1 to 4 carbon atoms, ethoxy groups and halogenated aryls. The additive may be employed in very small quantities (as low as 0.05 gram/liter).

The present invention relates to improvements in the production of electrodeposits, wherein the addition of certain agents to an aqueous acidic bath, in particular a nickel plating solution, will produce electrodeposits of superior brilliance, level, ductility and adhesion.

It is known to modify nickel electroplating baths with brightening agents such as sulfonamides, sulfonimides, etc. The plating is conventionally expected to possess sufficient brightness to be satisfactorily employable, ability to show all its surface imperfections filled in by the coating deposited thereon, and a good adhesion of the metal deposition upon the base metal especially while maintaining a desirably high degree of ductility. Furthermore, the plating should possess a satisfactory degree of throwing power and maintain a high receptivity to subsequent platings.

Various types of plating bath compositions are known for the bright plating of metals. Heretofore, the abovementioned properties of the end product have been only partially improved by the introduction into the plating bath mixture of brighteners. A large number of organic or inorganic materials have been used as brighteners but such brighteners are often only effective with certain metals other than nickel or have certain disadvantages which lead to difficulties when all of the abovementioned desired properties have to be enhanced and/or maintained to a satisfactory degree.

A conventional plating bath for nickel, for example, generally consists of an aqueous acid solution of nickel sulfate or nickel chloride or a mixture of the two, a buffer compound such as boric acid or formic acid or nickel fluoborate, and sometimes other salts such as ammonium chloride, sodium sulfate, magnesium sulfate solutions, and the like. The bath is kept at temperatures of usually 75 to 160° F. depending on the particular composition of the bath and the current density employed in the plating process may range anywhere from 0.5 to 100 amperes per square foot. The following bath composition and operating conditions are typical of the art:

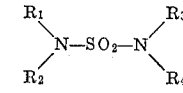
$NiSO_4 \cdot 7H_2O$	g./l.	300
$NiCl_2 \cdot 6H_2O$	g./l.	45
H_3BO_3	g./l.	40
Temperature	° F.	75
pH of solution		2–6
Current density	amps/ft.	10–75

To the above typical bath solution, and for that matter to all other similar composition described, for example, in U.S. Patent 2,523,191 to H. Brown, additives are added to improve the properties of the products, namely, the levelling power (or ability to fill in surface imperfections in the base metal) the brightness of the deposition, the adhesion of the coating, the ductility of the coated base metal, the throwing power of the deposited coating, the receptivity of the product to subsequent plating.

Additives such as allyl sulfonic acid, chloroalkyl sulfonic acid, reaction products of soluble acetylenic compounds having from 2 to 15 carbon atoms, condensation products of unsaturated aldehydes, and compounds containing the group —SO_2N= are all known and described in the literature. They, admittedly, either alone or in combination with auxiliary additives improve some of the above-mentioned prerequisites of a product but not a satisfactorily sufficient number of them to render the product commercially excelling.

It is, therefore, the main object of the present invention to provide an additive to be employed in electrodeposition of nickel to obtain an extremely satisfactory deposit having all of the above-mentioned properties.

The additive of this invention to be used in conjunction with conventional nickel plating bath solutions, is an unsaturated organic compound having the general empirical formula:



wherein R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen (to a maximum of three substitutions), unsaturated alkyls having at least 2 but not more than 6 carbon atoms, aryls, aralkyls, alkaryls, R—SO_3 radicals wherein R has from 1 to 4 carbon atoms, ethoxy groups and halogenated aryls.

It has been found that, besides obtaining over-all superior properties of the product (brighteness, levelling power, adhesion, ductility, throwing power, receptivity to plating), considerably minor amounts of the additive may be employed while maintaining a high degree of tolerance to metal contaminations of the solutions. Using the specific bath composition mentioned hereabove, quantities of the additive of the invention as low as 0.05 gram per liter of solution may be effectively employed. Generally, amounts of 1 gram per liter have been found to be ample.

The following are examples which illustrate the present invention.

EXAMPLE I

One liter of an aqueous nickel plating bath of the following composition was prepared:

	Grams
$NiSO_4 \cdot 7H_2O$	300
$NiCl_2 \cdot 6H_2O$	45
Boric acid	40

To this solution were added 0.9 gram of monoallyl sulfamide and the bath was employed to nickel plate a precleaned steel base at 140° F. a pH of 4.2 and at a current density of 40 amperes per square foot. A nickel plate was obtained which showed an exceptionally good levelling of the surface imperfections, was extremely bright, had excellent adhesion of the coating even when bent into a U-shaped form, showed very high throwing power and was found to be highly receptive to subsequent plating operations.

EXAMPLE II

To one liter of the basic solution of Example I was added 1 gram of diallyl sulfamide and the bath was em-

ployed to nickel plate a precleaned steel base at 140° F. a pH of 4.0 and at a current density of 40 amps/square foot. Substantially equal results were obtained as when using the additive of Example I.

The various additives of the present invention need not be employed alone, but may be used in conjunction with other additives or brighteners. These auxiliary or secondary brighteners may be conventional or those of the present invention. Obviously, the results obtained may be, often, superior with respect to some of the properties. However, this is not always the case, that is, no synergistic or even additive effect are sometimes achieved. Results substantially equal to those of Example I were obtained in the following example.

EXAMPLE III

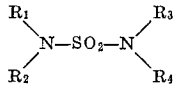
To one liter of the basic solution of Example I were added 0.9 gram of monoallyl sulfamide, 2.0 grams of benzene sulfamide and, as a secondary brightener, 0.1 gram of 2-butyne-1, 4-diol and the bath was employed to nickel plate a precleaned steel base at 140° F., a pH of 4.2 and at a current density of 40 amps/square foot. The results obtained were, when compared with those of Example I, well within the expectations and clearly superior to those of the prior art upon comparison with baths containing, for example, allyl sulfonic acid brighteners or conventional sulfamides.

The conditions of the baths will vary within certain limits which are recognized as being suitable for the purpose by any person skilled in the art. Thus, for example, the temperature of the bath may vary between 75° F. and 160° F., the pH of the solution may range from 1 to 6 depending on the basic bath constituents, and the current density during the electrodeposition may be of the order of 0.5 to 100 amperes per square foot.

Although the illustrative examples have been directed to the electroplating of nickel, it should be understood that the present inventive brightener is equally applicable to the electroplating of copper upon a metal base. The same process conditions and concentrations in the acidic bath are employed when copper is to be electrodeposited.

What is claimed is:

1. A bath for electrodepositing nickel comprising in an aqueous acid solution a material selected from the group consisting of nickel chloride, nickel sulfate, nickel fluoborate, and mixtures thereof, said solution having also dissolved therein an organic compound having the empirical formula



wherein R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen (to a maximum of three substitutions), unsaturated alkyls having from 2 to 6 carbon atoms, benzene rings, R—SO_3 radicals wherein R has from 1 to 4 carbon atoms, and ethoxy groups, said organic compound having a concentration in the aqueous acid solution ranging between about 0.05 gram per liter and saturation.

2. A bath according to claim **1** wherein said organic compound has a concentration in the aqueous acid solution ranging between about 0.05 gram per liter and 1.00 gram per liter.

3. A bath according to claim **1** wherein said organic compound is monoallyl sulfamide.

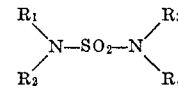
4. A bath according to claim **1** wherein said organic compound is diallyl sulfamide.

5. A bath according to claim **1** wherein two of the R's selected from the group consisting of R_1, R_2, R_3 and R_4 are hydrogen and two others are benzene rings.

6. A bath according to claim **1** wherein said organic compound is employed in conjunction with other commonly known bath brighteners.

7. A bath according to claim **6**, wherein said other commonly known bath brightener is 2-butyne-1,4-diol.

8. The process of electrodepositing nickel onto a base metal which comprises preparing an aqueous acidic solution consisting of (a) a nickel compound selected from the group consisting of nickel chloride, nickel sulfate, mixtures of nickel chloride and sulfate, nickel chloride and fluoborate, nickel sulfate and fluoborate, and nickel chloride, sulfate, and fluoborate, (b) an organic compound having the empirical general formula



wherein R_1, R_2, R_3 and R_4 are selected from the group consisting of hydrogen (to a maximum of three substitutions), unsaturated alkyls having from 2 to 6 carbon atoms, benzene rings, R—SO_3 radicals wherein R has from 1 to 4 carbon atoms, and ethoxy groups, said organic compound being present in a concentration of between 0.05 g./l. and saturation and electroplating the metal base at from 75 to 160° F., at a pH of 1 to 6 and at a current density of 0.5 to 100 amperes per square foot in said solution.

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JOHN H. MACK, *Primary Examiner.*

G. KAPLAN, *Assistant Examiner.*