United States Patent Office 3,130,135 Patented Apr. 21, 1964

3,130,135

NICKEL PLATING

Harry Axel Herman Ericson, Stockholm, Sweden, assignor by mesne assignments, to Firma Sture Granberger, Bochum, Germany, a firm

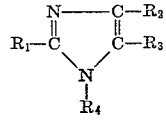
No Drawing. Filed Nov. 21, 1962, Ser. No. 239,329
Claims priority, application Sweden Nov. 21, 1961
6 Claims. (Cl. 204—49)

The invention relates to a bath for electrolytic deposition of nickel coatings having high brightness and good ductility, and to a process of nickel plating by using this bath.

A great number of brightening organic additives employed in nickel plating contain C=N groups, among which imidazol compounds are found. The imidazol compounds normally may be referred to brighteners of the second class or levellers, and are in such case used together with brighteners of the first class or carriers.

Conventional brighteners of the imidazol type show, however, in almost all cases a tendency of effecting brittle nickel deposits with low ductility. As the conventional brighteners, moreover, have a poor surface levelling action, it is only with difficulty possible to obtain brightness on a dull or ground basic surface.

It has now proved possible to produce nickel coatings with high brightness and good ductility by employing nickel plating baths containing an imidazol compound of the formula



wherein R_1 is hydrogen, an aliphatic or cyclic, saturated or unsaturated hydrocarbon radical or —A—R_5 whereof A designates an unsaturated aliphatic bridge and R_5 an aromatic radical, a double or triple bond in R_1 preferably being conjugated with the double bond at the carbon atom in the 2-position of the imidazol nucleus, and wherein R_2 and R_3 are hydrogen, aliphatic or cyclic, saturated or unsaturated hydrocarbon radicals and R_4 is hydrogen and —A—R_6 wherein A is an aliphatic bridge and R_6 is aliphatic and cyclic, saturated and unsaturated hydrocarbon radicals or an aliphatic radical containing one or several amino groups, or an alkoxy group, at least one of R_1 and R_4 being an unsaturated radical, preferably an unsaturated aliphatic radical.

In one embodiment of the invention, the said new brighteners of imidazol type have, thus, in the 2-position a substituent with one or several double or triple bonds, one of these bonds preferably being in conjugated position to the double bond in the 2-position of the imidazol nucleus. The said substituents in the 2-position are preferably alkenyl or alkynyl groups containing up to 6 carbon atoms. The cyclic hydrocarbon radical contemplated as R_1 is preferably aromatic, as for example a phenyl group. When the substituent in the 2-position is an unsaturated, aliphatic radical with more than one unsaturated bond, it probably includes more than 6 carbon atoms, for example in the case of two double bonds up to 12 carbon atoms or more. When the substituent in the 2-position is an unsaturated aliphatic bridge having an aromatic radical attached thereto, the aliphatic bridge preferably is a radical containing at maximum 6 carbon atoms, and the aromatic radical consists preferably of a phenyl group. The said substituents in the 2-position may contain groups rendering the compound more water soluble, for example sulphonic or carboxylic groups.

The substituents in the 4- and 5-position of the imidazol ring are preferably hydrogen atoms or methyl groups, but may also be other unsaturated or saturated hydrocarbon radicals, such as alkyl groups containing, for example, up to 4 carbon atoms. The substituent groups in the 4- and 5-position may be of same or different type. If they are not hydrogen or methyl groups, they are preferably the same unsaturated groups as indicated for R_1.

The substituent in the 3-position of the imidazol ring is preferably hydrogen, but may also be a saturated or unsaturated hydrocarbon radical, such as an alkyl, alkenyl, alkynyl or alkoxy group, above all such groups having at maximum 6 carbon atoms, or an amino containing group, for example an amino alkyl group, such as an amino ethyl or amino propyl group. Other amino containing groups may be amino alkyl-amino alkyl groups wherein alkyl preferably consists of methyl or ethyl, a piperazinyl group or groups containing 3 or 4 amino groups attached to each other by means of methylene or ethylene groups. A cyclic radical as substituent in 3-position is normally heterocyclic or aromatic.

In the bath according to the invention, the new brighteners are active in very low concentrations and may, for example, be applied in a concentration as low as 0.001 g./litre. They are preferably applied in a concentration not exceeding 0.1 g./litre.

The process according to the invention is carried out in a manner known for nickel plating metal objects, but with a bath containing a brightener described above.

With respect to their brightening and above all their surface levelling action, the new brighteners are highly superior to the simple imidazol compounds. In addition, the nickel deposits obtained show improved ductility. For obtaining the highest degree of freedom of stress in the coating in combination with brightest ductility, the new brighteners are combined with brighteners of the first class, usually aromatic sulphur compounds, such as sodium benzene disulphonate, sodium naphthalene trisulphonate, sulphonamides, sulphonimides, and the like. The new brighteners are excellently to incorporate in most of the bright nickel plating baths known per se, for example acid aqueous baths containing at least one nickel salt. The nickel plating bath may, for example, be of sulphate, chloride, fluoborate or sulphamate type.

The said new brighteners are new chemical compounds which are preferably synthetized in a manner analogous with that used for unsubstituted imidazol. If desired, an unsubstituted or partially imidazol may be substituted in a manner known per se.

The invention is illustrated by way of the following examples.

Example 1

A nickel plating bath of the following composition is prepared and applied at the current densities and temperatures as indicated in the table below:

Nickel sulphate	g./l.	300
Nickel chloride	g./l.	60
Boric acid	g./l.	40
Sodium naphthalene trisulphonate	g./l.	15
2-propenyl-imidazol	g./l.	0.01
pH		3.5–5.0
Current density	a./dm.^{2}	2–8
Temperature	° C.	45–60

It has proved desirable to keep the nickel plating bath moving while the nickel deposition is going on. Hereby a uniform and highly satisfactory bright coating over the entire plate is obtained.

Example 2

In this experiment a nickel plating bath of the below

composition is used at the current densities and temperatures as indicated in the following table.

Nickel sulphate	g./l.	300
Nickel chloride	g./l.	60
Boric acid	g./l.	40
Sodium naphthalene trisulphonate	g./l.	15
2-ethynyl-imidazol	g./l.	0.01
pH		3.5–5.0
Current density	a./dm.^{2}	2–8
Temperature	° C.	45–60

Even in this example stirring of the nickel plating bath during the deposition of nickel proved desirable. The nickel coating obtained is even in this case of uniform and good brightness as well as of good ductility.

Example 3

In this example, the nickel plating bath had the composition and was used at the current densities and temperatures as they appear from the table below.

Nickel sulphate	g./l.	300
Nickel chloride	g./l.	60
Boric acid	g./l.	40
Sodium naphthalene trisulphonate	g./l.	15
2-vinyl-imidazol	g./l.	0.01
pH		3.5–5.0
Current density	a./dm.^{2}	2–8
Temperature	° C.	45–60

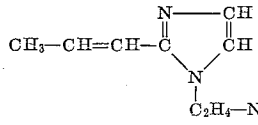
Even in this case it proved desirable to stir the nickel plating bath while the nickel deposition was going on. The brightness obtained was uniform and good over the entire plate and the nickel deposit showed good ductility.

Example 4

In this experiment a nickel plating bath was used which had the composition as follows:

Nickel sulphate	g./l.	300
Nickel chloride	g./l.	60
Boric acid	g./l.	40
Sodium naphthalene trisulphonate	g./l.	15
p-Benzoic acid sulphonimide, sodium salt	g./l.	0.5
Imidazol brightener according to the invention	g./l.	0.001
Sodium lauryl sulphate	g./l.	0.25

The imidazol brightener applied in this example was 2-propenyl-3-diethylenediamin-imidazol having the formula:



During the nickel plating experiment, the nickel plating bath which had a pH of 3.5–5 and a temperature of 45–65° C. was stirred. The current density during the experiment was 2–8 a./dm.^{2}. The nickel coating obtained showed uniform and good brightness as well as good ductility.

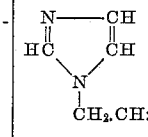
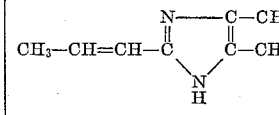
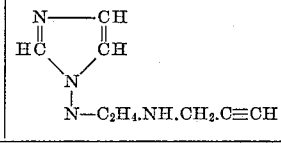
Example 5

The experiment as carried out in Example 4 was repeated under the conditions indicated, with the exception, however, that as imidazol brightener was used 2-(β-phenylethenyl)-3-(β-hydroxyethyl) - imidazol in an amount of 0.02 g./l. The nickel deposit resulting from this experiment showed uniform and good brightness over the entire plate.

Examples 6–12

The experiment as carried out in Example 4 was repeated under the conditions indicated, the nickel plating bath having the composition as defined in Example 4, with the exception, however, that as imidazol brightener 0.01 g./l. of the imidazols as listed in the table below

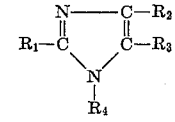
was used. In some examples, the structural formula of the imidazol used is shown.

Example No.	Imidazol brightener	Formula
6	3-propynyl-imidazol	
7	2-propenyl-3-(β-hydroxyethyl)-imidazol.	
8	3-propenyl-imidazol	
9	2-propenyl-3-aminoethyl-imidazol.	
10	2-propenyl-3-butyl-imidazol.	
11	2-propenyl-4,5-dimethyl-imidazol.	
12	3-propynylamino-ethyl-imidazol.	

The nickel deposits obtained by these experiments showed good ductility and uniform as well as good brightness.

What I claim is:

1. Nickel plating bath containing at least one nickel salt as a source of nickel and as a brightener, an imidazol compound having the formula

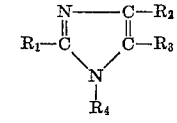


wherein R_1 is selected from the group consisting of hydrogen and —A—R_5, A being an aliphatic bridge and R_5 being selected from the group consisting of unsaturated and saturated, aliphatic and cyclic radicals, and aromatic radicals; wherein R_2 and R_3 are selected from the group consisting of hydrogen, aliphatic and cyclic, saturated and unsaturated hydrocarbon radicals; and wherein R_4 is selected from the group consisting of hydrogen and —A—R_6, A being an aliphatic bridge and R_6 being selected from the group consisting of aliphatic and cyclic, saturated and unsaturated hydrocarbon radicals and aliphatic radicals bearing at least one amino group, and alkoxy groups; at least one of R_5 and R_6 being present and at least one of R_1 and R_4 being an unsaturated radical; said brightener being provided in an amount of 0.001 to 0.1 gram/liter.

2. Nickel plating bath according to claim 1 wherein a double bond in R_1 is conjugated with the double bond at the carbon atom of the 2-position of the imidazol nucleus.

3. Nickel plating bath according to claim 1 wherein a triple bond in R_1 is conjugated with the double bond at the carbon atom of the 2-position of the imidazol nucleus.

4. Process for nickel plating comprising electrodepositing nickel from a bath containing at least one nickel salt as a source of nickel and as a brightener, an imidazol compound having the formula



wherein R_1 is selected from the group consisting of hydrogen and —A—R_5, A being an aliphatic bridge and R_5 being selected from the group consisting of unsaturated and saturated, aliphatic and cyclic radicals and aromatic

radicals; wherein R_2 and R_3 are selected from the group consisting of hydrogen, aliphatic and cyclic, saturated and unsaturated hydrocarbon radicals; and wherein R_4 is selected from the group consisting of hydrogen and —A—R_6, A being an aliphatic bridge and R_6 being selected from the group consisting of aliphatic and cyclic, saturated and unsaturated hydrocarbon radicals and aliphatic radicals bearing at least one amino group, and alkoxy groups; at least one of R_5 and R_6 being present and at least one of R_1 and R_4 being an unsaturated radical; said brightener being provided in an amount of 0.001 to 0.1 gram/liter.

5. Process for nickel plating according to claim 4 wherein a double bond in R_1 is conjugated with the double bond at the carbon atom of the 2-position of the imidazol nucleus.

6. Process for nickel plating according to claim 4 wherein a triple bond in R_1 is conjugated with the double bond at the carbon atom of the 2-position of the imidazol nucleus.

References Cited in the file of this patent

UNITED STATES PATENTS

2,684,327	Passal	July 20, 1954
2,737,484	Passal	Mar. 6, 1956
2,905,692	Paleveda et al.	Sept. 22, 1959
2,986,500	Passal	May 30, 1961
3,037,028	Green	May 29, 1962
3,054,733	Heiling	Sept. 18, 1962