

## UNITED STATES PATENT OFFICE

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BRIGHT NICKEL PLATING COMPOSITION  
AND PROCESS

Harold George Donnelly, Dearborn, Mich., as-  
signor to Wagner Brothers, Inc., Detroit, Mich.,  
a corporation of Michigan

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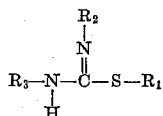
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This invention relates to the electrodeposition of nickel and is more particularly concerned with a bright nickel plating bath, having, as an additive, therein a compound containing an isothioureido radical, and with a process utilizing such a bath.

It has been proposed that various agents be added to nickel plating baths to avoid pitting and brittleness in the nickel coating. Among these may be mentioned arylsulfonic acids, aryl-naphthalenic acids, gum tragacanth, sulfonated resins, oleo resins, et cetera. By introducing such agents into the bath, hydrogen atoms formed by hydrolysis are more quickly loosened from the surface of the metal thereby affording a smooth plating surface. However, the addition of such agents to the bath has not satisfactorily overcome the problem of brittleness and leaves much to be desired from the standpoint of brightness.

It is therefore a principal object of the present invention to provide a novel group of addition agents for a nickel plating bath which allows the bath, under specified conditions, to plate out a bright, non-brittle, non-pitted, coat of nickel. A further object of the present invention is to provide a group of compounds which accomplishes the herein-described results without decomposition of the agent, in situ. Still another object of the present invention is to provide an addition agent for a nickel plating bath which has an isothioureido nucleus contained therein. Other objects will become apparent hereinafter.

I have now found that the addition of a compound, as hereinafter described, to a conventional nickel plating bath, not only greatly enhances the quality, particularly the brightness and ductility, of a plate resulting from the use thereof, but the agent is apparently not decomposed by electrolysis, thereby avoiding the necessity of frequent replacement. Additaments of the present invention are at least partially water-soluble organic compounds containing an isothioureido nucleus, having an organic radical attached to the sulphur atom of the nucleus, and have the following formula:



wherein  $R_1$  is an alkanolic acid, amide, substituted amide, ester, acid salt, alkanol, alkylamine acid addition salt, or alkylamine quaternary ammonium salt, wherein  $R_2$  and  $R_3$  are hydrogen or an organic radical, and wherein  $R_2$  and  $R_3$  may be

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the same, different, or joined together to form a heterocyclic ring-structure.

Thus,  $R_1$  may be a radical such as, for example, acetic acid, propionic acid, butyric acid, acetamide, propionamide,  $N,N$ -dimethylacetamide,  $N,N$ -diethylpropionamide, methyl acetate, ethyl propionate, propyl butyrate, ethyl acetate, benzyl acetate, sodium acetate, potassium propionate, calcium acetate, lithium butyrate, ethanol, isopropanol, propanol, methanol,  $n$ -butanol, isobutanol, tertiary butanol, pentanol, ethyl amine hydrochloride, propylamine hydrobromide, butylamine hydriodide,  $N,N$ -dimethylethylamide methobromide, et cetera, while  $R_2$  and  $R_3$  may be hydrogen atoms, or similar or dissimilar organic radicals, such as, for example, alkyl as methyl, ethyl, propyl, isopropyl, normal-butyl, isobutyl, secondary butyl, normal-pentyl, isopentyl, secondary pentyl, tertiary pentyl, et cetera; alkenyl as vinyl, allyl, methallyl, crotyl, et cetera; aryl as phenyl, naphthyl, dipropyl-naphthyl, benzyl, naphthyl-butyl, et cetera; aralkenyl as vinyl-phenyl, crotonyl-naphthyl, methallyl-phenyl, naphthyl-allyl, et cetera; cycloparaffinic as cyclopentyl, ethyl-cyclohexyl, tributyl-cyclohexyl, et cetera; cyclo-olefinic as cyclopentenyl, cyclohexenyl, et cetera; heterocyclic as thienyl, pyrrolyl, furyl, et cetera. These radicals may have one or more of their hydrogen atoms substituted with other elements or groups as halogen, hydroxyl, nitro, sulfo, et cetera. Further, the two nitrogen atoms of the isthioureido radical may be joined with other atoms to form a heterocyclic radical, such as pyrazole, imidazole, oxatriazine, oxadiazine, et cetera. Representative compounds which are contemplated within the scope of the above-mentioned formula include, among others, beta-isothioureidopropionic acid, isothioureidoacetamide, ethyl alpha-( $N$ -methyl- $N'$ -phenyl-isothioureido)-butyrate, sodium  $N$ -benzyl- $N'$ -hexyl-beta-isothioureidopropanol,  $S$ -(2-pyrimido)-beta-mercaptopropionic acid, sodium  $S$ -(2-pyrimido)-mercaptoacetate,  $S$ -(4-methyl-5-ethyl-2-pyrimido)-beta-mercaptopropionamide, et cetera.

Although the addition of the additives above-described to the plating bath enhances the plating ability of any type of bright nickel bath, a Watts type bath is particularly adaptable to this additament. Usually, both nickel chloride and nickel sulfate are used as the source of metallic ions. A wetting agent, such as sodium lauryl sulfate, benzene sulfonic acid, sulfonated long-chain fatty acid esters, et cetera, may be used in an amount of less than one percent, and preferably

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about 0.01 percent. A buffer such as boric acid, et cetera, in an amount sufficient to maintain the pH of the bath in the range of 2.5 to 5.5 is also employed. The temperature may be varied between 60 and 175 degrees Fahrenheit with satisfactory results, however, temperatures between 140 and 160 degrees Fahrenheit are preferred. Although a current density between 50 and 75 amperes per square foot is apparently the most desirable, densities between 25 and 100 amperes per square foot may be used satisfactorily.

It is to be understood that various other additives known to the art, in addition to those compounds herein-described, may also be employed, however, I have found that such additives do not greatly enhance the plating ability of the bath, and a preferred embodiment of the present invention includes only those above-mentioned. An isothioureido compound, as defined hereinbefore, is usually employed in an amount between about 0.01 and about 0.1 percent, while 0.025 percent is the preferred amount.

The following examples are given to illustrate the practice of the present invention, but are not to be construed as limiting.

#### Example 1. Watts type bath

A solution was prepared containing 33.5 ounces of nickel sulfate hexahydrate, 6.4 ounces of nickel chloride, 4.6 ounces of boric acid, and 0.025 ounce of beta-isothioureidopropionic acid per gallon. The temperature of the bath was raised to about 150 degrees Fahrenheit, the pH maintained at about 5 and varying current densities passed therethrough. Lustrous, bright panels were obtained at current densities up to and through the 120 amperes per square foot range. This result may be contrasted to the electro-deposited coatings obtained when no additive is employed, which are dark grey and hazy at current densities above 15 amperes per square foot.

#### Example 2

The following additaments may be used in place of beta-isothioureidopropionic acid of the bath in Example 1: alpha-isothioureidopropionic acid, sodium beta-isothioureidopropionate, potassium alpha-isothioureidopropionate, methyl-gamma-isothioureidobutyrate, alpha-isothioureidoacetamide, beta-isothioureidoacetamide, beta-isothioureidopropionamide, beta-[N-methyl-N'-(p-methoxyphenyl) - isothioureido] - N,N-dimethylpropionamide, beta-isothioureidopropanol, beta-isothioureidopropylamide hydrochloride, beta-isothioureidopropyl-dimethylamine methiodide. The results obtained all represent an improvement over the art, with the efficacies of the particular compounds varying.

#### Example 3. Combined type bath

A solution was prepared containing:

|                                                 | Ounces/gallon |
|-------------------------------------------------|---------------|
| $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ ----- | 25.1          |
| $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ----- | 20.9          |
| Boric acid -----                                | 3.9           |
| Beta-isothioureidopropionic acid -----          | 0.033         |
| pH (electrometric) -----                        | 5.0           |

The bath was tested in a manner exactly similar to that of Example 1. Test panels obtained were lustrous, bright through the 100 amperes per square foot range.

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#### Example 4. All chloride bath

A solution was prepared containing:

|                                                   | Ounces/gallon |
|---------------------------------------------------|---------------|
| 5 $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ----- | 35.9          |
| Boric acid -----                                  | 3.1           |
| Beta-isothioureidopropionic acid -----            | 0.038         |
| pH (electrometric) -----                          | 5.0           |

10 The bath was tested in a manner exactly similar to that of Example 1. Test panels obtained were lustrous bright through the 85 amperes per square foot range.

#### Example 5

15 Other additaments which have been tested and found as satisfactory as those described above include ethyl beta-isothioureidopropionate and beta-isothioureidopropionamide.

20 Various modifications may be made in the method of the present invention without departing from the spirit or scope thereof, and it is to be understood that I limit myself only as defined in the appended claims.

I claim:

25 1. An acid aqueous nickel plating bath containing nickel salts, an acid buffering agent, and an at least partially water-soluble organic compound containing an isothioureido nucleus and having an organic radical attached to the sulphur atom of the nucleus, said organic compound being dissolved in said bath in sufficient quantity to produce bright nickel plating therefrom.

30 2. The method which includes: electrodepositing nickel from an aqueous, acid nickel salt solution having dissolved therein an at least partially water soluble organic compound containing an isothioureido nucleus and having an organic radical attached to the sulphur atom of the nucleus, said organic compound being dissolved in said bath in sufficient quantity to produce bright nickel plating therefrom.

35 3. The process which includes: electrodepositing nickel from an aqueous, acid nickel salt solution, having dissolved therein between 0.01 percent and 0.1 percent of beta-isothioureidopropionic acid.

40 4. An acid nickel plating bath, comprising: an aqueous solution of nickel salts and between 0.01 percent and 0.1 percent beta-isothioureidopropionic acid.

50 5. A Watts type nickel plating bath containing as an additive therein, between 0.01 and 0.1 percent beta-isothioureidopropionic acid.

6. An acid nickel plating bath, comprising: 55 an aqueous solution of nickel salts and between 0.01 percent and 0.1 percent ethyl beta-isothioureidopropionate.

7. An acid nickel plating bath, comprising: an aqueous solution of nickel salts and between 60 0.01 percent and 0.1 percent beta-isothioureidopropionamide.

8. The method which includes: electrodepositing nickel from an aqueous, acid nickel salt solution, having a pH between about 2.5 and about 5.5, maintained at a temperature between about 60 and about 175 degrees Fahrenheit, and containing dissolved therein between 0.01 and 0.1 percent of an at least partially water-soluble organic compound containing an isothioureido nucleus having an organic radical attached to the sulphur atom of the nucleus, by passing a current having a density between about 25 and about 100 amperes per square foot.

75 9. A nickel plating bath containing soluble nickel salts, sufficient boric acid to buffer the

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solution at a pH of between about 2.5 and about 5.5, and between about 0.01 and 0.1 percent beta-isothioureidopropionic acid.

10. A nickel plating bath containing nickel salts, sufficient boric acid to buffer the solution at a pH of between about 2.5 and about 5.5, and between about 0.01 and 0.1 percent of an at least partially water-soluble organic compound containing an isothioureido nucleus and having an organic radical attached to the sulphur atom of the nucleus.

11. A nickel plating bath containing nickel chloride and nickel sulfate ions, less than about one percent of a wetting agent, an acid buffer sufficient to maintain the pH of the bath in the

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range between about 2.5 and about 5.5, and between 0.01 percent and 0.1 percent beta-isothioureidopropionic acid.

HAROLD GEORGE DONNELLY.

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