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3,203,787

METHOD OF AND COMPOSITION FOR CHEMICALLY DISSOLVING ELECTROLESS METAL DEPOSITS

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This invention relates to dissolving, by chemical action, certain types of metal deposits and more particularly so-called electroless nickel deposits on various basis metals and especially copper and copper alloy basis metals. More particularly the invention relates to bath compositions for dissolving the aforesaid electroless deposits, and to methods of using those compositions without adversely affecting the basis or substrate metal.

During the past decade, a new type of metal deposit has been commercially developed which is termed "electroless" inasmuch as no external electrical potential is employed in producing such deposits. A method of and compositions for producing electroless deposits of nickel are disclosed, for example, in U.S. Patent 2,532,283. These deposits differ from nickel coatings obtained by conventional electroplating processes, notably in that the former contain a certain amount of phosphorus, thus forming a nickel-phosphorus alloy deposit. These electroless coatings exhibit the structure of an amorphous substance with liquid-like arrangement of the atoms. They are extremely resistant to attack in various corrosive media.

It is often desirable in industrial operations to reclaim plated objects that have been rejected because of unsatisfactory finish. Reclamation of electroplated components is ordinarily achieved by immersing the defective object in a solution formulated selectively to remove the deposited plate or coating without affecting the substrate metal. In any stripping operation such as this it is important that no dimensional change be caused in the substrate metal during the stripping operation in order that the part can be replated without further mechanical preparation. Usually, parts plated with electroless nickel or cobalt are of very intricate shape and are costly. Therefore, a method permitting salvage of rejects in such cases is especially important.

A number of satisfactory proprietary formulations are available for chemically dissolving all or most of the commercially known electrically deposited coatings from a variety of basis metals. However, so far as I am aware, no formulations are available for recovering rejected parts plated with electroless nickel on copper or copper-alloy components; that is, none are available which do not simultaneously attack such basis metals and cause total loss of the part.

Heretofore, it has been possible to remove electroless nickel deposits from copper, brass, bronze and other cuprous alloys only by immersing the components in aqueous solutions containing nitric acid, or alternatively by mechanically grinding the surface. Both of these treatments dimensionally affect the basis metals, making such treatments uneconomical and unsuitable for salvaging purposes.

A primary object of the present invention, therefore, is the provision of a solution and a method for dissolving chemically deposited (electroless) nickel coatings, particularly from copper and copper alloy basis metal components, without adversely affecting the surface and physical dimensions of the basis metal.

It is a further object to effect the removal of the deposited coatings rapidly and economically, whereby the

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salvage value of the reclaimed parts will be substantially increased.

Another object is to provide compositions, and a process utilizing these, for removing electroless deposits of nickel in a safe and convenient manner, wherein the compositions remain stable during storage and in use, and wherein the process does not require close, critical control in order to obtain commercially satisfactory results.

In brief, the invention comprehends the provision of a bath for selectively dissolving electroless nickel deposits from copper or copper alloy basis metals, wherein the bath comprises a ternary system consisting essentially of an aqueous solution of an alkali metal hydroxide, a nitro-substituted aromatic compound and a primary aliphatic polyamine. In each case, the component selected from the foregoing groups in the system may comprise a mixture of available members in each such group.

Removal of the electroless nickel coatings is effected simply by immersion of the plated components in the foregoing bath. The bath is desirably maintained at a temperature of at least 150° F., but may be operated at any temperature up to its boiling point. Optimum results are obtained at temperatures of from 170° to 180° F. Complete removal of the deposit results usually within 5 to 15 minutes depending on bath temperature and thickness of deposit. No electric current is required and stripping is achieved without corroding the substrate metal.

It is essential to the operability of the foregoing solutions and process that the bath be highly alkaline, substantially more so than is naturally produced by the presence of the amine compounds themselves. It is believed that the high alkalinity of the novel system, as obtained by the addition of the alkali metal hydroxide, acts as a "solvent" for the phosphorus contained in the electroless nickel deposit and the solubilization of this phosphorus is the rate-controlling factor during the dissolution of the chemically plated alloys.

Acid stripping solutions disclosed by the prior art for selectively removing electroplated nickel coatings from copper and copper base alloys, without damaging the substrate metal, are unsuitable in the case of the electroless deposits. Thus, the prior art method of immersing nicklecoated objects in a sulfuric acid solution and then making these objects anodic by the application of a suitable electric potential, is virtually useless and is commercially impractical for stripping electroless nickel deposits.

Similarly, other formulations available for removing electroplated deposits, where these formulations contain cyanide compounds, are very corrosive to copper and copper alloys and are thus unsuitable for the purposes of this invention.

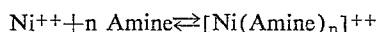
It is interesting to note also that a binary system employing nitro aromatic derivatives and polyamines found useful in this invention, but wherein the alkali metal hydroxide is omitted, will successfully remove ordinary electroplated metal films, including nickel. But such a binary system is quite inoperative for removing the electroless deposits here concerned.

Aromatic compounds suitable for this invention are the nitro benzene and nitro naphthalene derivatives which are readily soluble in strong alkaline solution, wherein there is at least one nitro group attached to the aromatic nucleus, and where the nucleus also carries an additional radical having a water-solubilizing and/or activating effect on the derivative as a whole. Suitable compounds in this class include: nitrobenzene sulfonic acid, nitrobenzoic acid, nitrochlorobenzene, nitroaniline, nitrophenol and mixtures thereof; also the alkali metal salts of the

acids in the foregoing group. The several ortho, para and meta isomers of these nitro derivatives are operative singly or in admixture, but the m-nitro compounds by themselves appear most efficient in practical operation. The soluble naphthylenic equivalents of the foregoing benzene compounds are also operative although presently not preferred because of economic reasons. Optimum results, both operationally and economically are obtained with the nitro benzene sulfonic and nitro benzoic acids.

The concentration of these nitro derivatives in solutions of this invention ranges from 0.1 to 1.0 mole per liter.

The useful aliphatic polyamines are those exhibiting a strong complexing ability for nickel and cobalt ions. The formation of the complex is represented by the following reaction:



The complexing ability of the amine is expressed by the equilibrium constant K for this reaction, where

$$K = \frac{[\text{Ni}^{++}] \times [\text{Amine}]^n}{[\text{Ni}(\text{Amine})_n]^{++}}$$

For the polyamines of this invention, $K \leq 10^{-16}$. Generally speaking, secondary and tertiary amines do not appear to be operative, and the useful compounds are limited to the primary polyamines wherein the aliphatic radical has from 2 to 6 carbon atoms. Ethylenediamine is especially satisfactory, both from operational and cost standpoints. Diethylenetriamine and triethylenetetramine are also quite satisfactory. Again, these amines may be employed singly or in admixture, and their total concentration in solution should range from about 0.1 to 3.0 moles per liter.

The third component of the ternary system, namely the hydroxide, may consist of any of the alkali metal hydroxides to provide the high degree of alkalinity necessary in the bath. This is achieved by providing sufficient alkali such that the hydroxyl ion concentration in solution is within a range of 0.2 to 2.0 equivalents per liter. Thus it is apparent that an alkalinity substantially higher than that obtained in binary systems for removal of electroplated deposits is required in order to render the solution effective for removal of the electroless nickel deposits here concerned. This is illustrated further in the following examples.

The following examples show a number of solutions embodying the invention and are illustrative but not all-inclusive of the systems which may be employed in practicing the invention. Also, one example of a system outside the scope of the invention is given to illustrate the importance of the high alkalinity mentioned above.

Example 1

The following formulation illustrates a preferred embodiment of this invention:

	M./l.
Ethylenediamine	2.0
Sodium m-nitrobenzene sulfonate	0.25
Sodium hydroxide	1.5

A brass object plated with 0.0001" of electroless nickel was immersed in the foregoing solution at a temperature of 170–180° F. The nickel deposit was completely removed after 10–12 minutes of immersion, and the brass object showed no sign of attack or of dimensional change upon removal from the solution.

Example 2

The following aqueous solution, outside the scope of this invention, was prepared for purposes of comparison:

	M./l.
Ethylenediamine	2.0
Sodium m-nitrobenzene sulfonate	0.25

A brass object identical with that employed in Example 1 above and plated with the same thickness of electroless

nickel was immersed in this solution, again at a solution temperature of 170–180° F. The object was held in the solution for 2 hours. None of the nickel deposit was removed, nor was there any action of any sort visible, thus demonstrating the necessity of the high degree of alkalinity in order to obtain the desired result.

Example 3

The following aqueous solution falling within the scope of this invention was prepared:

	M./l.
Diethylenetriamine	2.0
Sodium m-nitrobenzoate	0.3
Sodium hydroxide	1.0

A copper object plated with 0.0001" of electroless nickel was immersed in this solution at 180° F and was completely stripped of the deposit in 8–10 minutes. The copper basis metal showed no sign of attack and was suitable for immediate replating after normal cleaning in conventional cleaning solutions.

Example 4

The following aqueous solution within the invention was also tried:

	M./l.
Triethylenetetramine	1.5
Sodium m-nitrosulfonate	0.25
Sodium hydroxide	1.0

An object plated with 0.0001" of electroless nickel, wherein the basis metal consisted of a steel-copper assembly, was completely stripped by immersion in the above solution for 7–10 minutes at a bath temperature of 170–180° F. Both the copper and steel basis metals were free of attack and were ready for replating immediately after conventional cleaning steps.

Similar results are obtained with electroless nickel deposits of all thicknesses within the limits normally encountered in practice, the time of immersion varying, of course, with the thickness of the deposit and the temperature of the solution.

As indicated in the examples given herein, the invention is operative for the removal of electroless nickel deposits from basis metals other than cuprous metals, and its use in such applications is therefore not excluded. Generally, however, other means are available for removing the deposits from basis metals other than cuprous which will be preferred. But the reverse of this is not true in that such other means are not satisfactory for copper and copper alloy basis metal.

The invention has been described in connection with certain preferred embodiments but it is to be understood that these are illustrative rather than restrictive, and that variants of the particularly named bath components may be employed within the limits described in the specification and defined in the following claims.

What is claimed is:

1. An aqueous bath for selectively dissolving electroless nickel deposits for exposed surfaces of a basis metal, which bath comprises a ternary system consisting essentially in addition to water of a member selected from each of the following groups, (a), (b) and (c): (a) at least one alkali metal hydroxide providing in aqueous solution a hydroxyl ion concentration of from 0.20 to 2.0 moles per liter; (b) an aromatic compound selected from the group consisting of nitrobenzene and nitronaphthalene derivative having at least one water-solubilizing radical in addition to the nitro radical attached to the aromatic nucleus, and mixtures thereof, such compound being present in solution at concentrations of from about 0.1 to 1.0 mole per liter; (c) at least one aliphatic primary polyamine wherein the aliphatic radical contains from two to six carbons, said aliphatic amine having strong complexing ability for nickel ions and being present in amount of about 0.1 to 3.0 moles per liter.

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2. An aqueous bath as defined in claim 1, wherein said alkali metal hydroxide is selected from the group consisting of sodium and potassium hydroxides.

3. An aqueous bath as defined in claim 1, wherein said aromatic compound is selected from the group consisting of sodium nitrobenzene sulfonate and sodium nitrobenzoate.

4. An aqueous bath as defined in claim 1, wherein said polyamine is selected from the group consisting of ethylenediamine, diethylenetriamine and triethylenetetramine.

5. An aqueous bath as defined in claim 1, wherein said ternary system consists of essentially 1.5 moles per liter of sodium hydroxide, 0.25 mole per liter of sodium m-nitrobenzene sulfonate, and 2.0 moles per liter of ethylenediamine.

6. A method of selectively dissolving electroless nickel deposits from exposed surfaces of a basis metal, which comprises providing an aqueous bath consisting essentially in addition to water of a member selected from each of the following groups (a), (b) and (c): (a) at least one alkali metal hydroxide in amount sufficient to provide in aqueous solution a hydroxyl ion concentration of from 0.2 to 2.0 moles per liter; (b) an aromatic compound selected from the group consisting of nitrobenzene and nitronaphthalene derivatives having at least one water-solubilizing radical in addition to the nitro radical attached to the aromatic nucleus, and mixtures thereof, such compound being present in solution at concentrations of from about 0.1 to 1.0 mole per liter; (c) at least one aliphatic primary polyamine wherein the aliphatic radical contains from two to six carbons, said aliphatic amine having strong complexing ability for nickel ions and being present in amount of from 0.1 to 3.0 moles per liter; maintaining said bath at a temperature above 150° F., immersing the plated basis metal in such bath for a time sufficient to remove the electroless deposit and then removing the depleted basis metal from the bath.

7. The method as defined in claim 6, wherein said

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alkali metal hydroxide is selected from the group consisting of sodium and potassium hydroxides.

8. The method as defined in claim 6, wherein said aromatic compound is selected from the group consisting of sodium nitrobenzene sulfonate and sodium nitrobenzoate.

9. The method as defined in claim 6, wherein said polyamine is selected from the group consisting of ethylenediamine, diethylenetriamine and triethylenetetramine.

10. The method of stripping electroless nickel deposits from copper and copper alloy basis metal which comprises providing an aqueous stripping bath consisting essentially in addition to water of approximately 1.5 moles per liter of sodium hydroxide, 0.25 mole per liter of sodium m-nitrobenzene sulfonate and 2.0 moles per liter of ethylenediamine, maintaining said bath at a temperature of approximately 170–180° F., immersing the plated metal in said bath for a sufficient time to remove the electroless deposit thereon and then removing the basis metal from the bath.

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