

[54] **NONAQUEOUS ELECTROLESS PLATING**
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[73] Assignee: **North American Rockwell Corporation**
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[57] ABSTRACT

A process for electroless plating of chromium, cadmium or copper wherein a salt of the metal is dissolved in a nonaqueous organic solvent and contacted with a catalytically active surface in the presence of a reducing agent to thereby reduce the salt and plate the surface with the metal.

[56] References Cited

UNITED STATES PATENTS

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10 Claims, No Drawings

NONAQUEOUS ELECTROLESS PLATING

BACKGROUND OF THE INVENTION

The electroless plating of metals from aqueous solution is known. For example, it is known to deposit chromium by a process wherein a metallic substrate is inserted in a bath containing a chromium salt in aqueous solution, a hypophosphite salt and a suitable buffering (pH controlling) agent. Chromium is deposited as a pure metal on the surface of the substrate. Another prior art chromium electroless plating solution includes sodium hypophosphite, sodium citrate and a mixture of chromium halides in aqueous solution. In addition to sodium hypophosphite, alkali metal borohydrides and boron compounds which carry one to four hydrogen atoms at the boron atom have also been used as reducing agents in plating baths for the production of metal coatings on metal or plastic surfaces. When an alkali metal borohydride is used as reducing agent, the electroless process is reportedly carried out in aqueous alkaline solution, often with the addition of complex formers such as ethanolamine, etc.

It is known that alkali metal borohydrides react spontaneously with aqueous solutions of nickel, cobalt or iron salts to form precipitates of the corresponding metal borides. The free metal may be plated on an appropriate catalytically active substrate by close pH control. It is also known that borohydrides precipitate nickel boride or cobalt boride from solvents such as absolute ethanol, methanol, isopropyl alcohol, isopropylamine, ethylenediamine, and pyridine. These precipitates may be coated on steel substrates and heated in reducing atmosphere to form an alloy containing nickel and boron on the steel (U. S. Pat. No. 2,726,170).

It is also known to plate amalgams by placing a soluble, chemically reducible compound of the metal to be plated (e.g., stannous chloride), a soluble chemically reducible compound of mercury (e.g., mercuric chloride) and a reducing agent (e.g., aluminum powder) directly on the metal surface to be plated and then applying a common solvent for the chemically reducible compounds. The solvent is ordinarily water although methyl and ethyl alcohols and other organic solvents are said to be operable. The plating is reported not to take place when a solution of the stannous and mercuric salts is first prepared (U.S. Pat. No. 3,049,437).

SUMMARY OF THE INVENTION

A process for electroless plating of chromium, cadmium or copper metal wherein a salt of the metal is dissolved in a nonaqueous organic solvent and contacted with catalytically active surface in the presence of a reducing agent to thereby reduce the salt and plate the surface with the metal.

An object of the present invention is the provision of a nonaqueous electroless plating process.

Further objects and advantages will become apparent upon reading the undergoing specification and claims.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

An electroless plating process is provided wherein a chromium, cadmium or copper metal salt is dissolved in a nonaqueous organic solvent and contacted with a catalytically active surface in the presence of a reducing agent and wherein the surface is plated with the corresponding free metal.

Suitable organic solvents are aliphatic ethers and heterocyclic amines. Suitable aliphatic ethers include acyclic ethers as well as cyclic ethers such as monocyclic alkylene ethers. Suitable acyclic ethers are alkylene ethers such as alkylene glycol alkyl ethers and particularly lower alkylene glycol lower alkyl ethers such as diethylene glycol dimethyl ether and ethylene glycol dimethyl ether. Suitable monocyclic alkylene ethers are alkylene oxides such as tetrahydrofuran. Particularly preferred monocyclic alkylene ethers are the lower alkylene oxides. Suitable heterocyclic amines include monocyclic 6-membered ring compounds containing one hetero-N-atom such as pyridine. The organic solvent should dissolve the metal salt, the reducing agent and the coproducts left after the

plating has occurred. The solvent should have low volatility and a high flash point and should provide a stable bath.

The reducing agent employed can be any boron compound which carries at least one hydrogen atom at the boron atom. Suitable inorganic boron compounds include borohydrides such as alkali metal borohydrides (e.g., lithium, sodium and potassium borohydride). Suitable organic boron compounds include alkoxy substituted borohydrides and particularly lower alkoxy substituted borohydrides and boranes such as amine boranes. An example of suitable aliphatic amine boranes are the alkyl substituted amine boranes such as trimethyl amine borane. Lower alkyl amine borane compounds are the particularly preferred amine boranes. Other suitable reducing agents are formaldehyde, hydrazine and reducing sugars such as glucose. The reducing agent should be dissolved in a nonaqueous organic solvent selected from the group of solvents listed above. It is not necessary, however, for both the metal salt and the reducing agent to be dissolved in the same solvent as long as the solvents are mutually miscible so that a homogeneous bath is formed.

The metals employed according to the present invention can be plated on any catalytically active surface. The expression "catalytically active surface" is intended to mean any surface which will catalyze the reduction of the salt of the metal employed to the corresponding free metal. Suitable surfaces include nickel and steel. The surface should be cleaned of any adherent oxide film prior to introduction into the plating bath.

Nonaqueous electroless plating possesses a number of distinct advantages over aqueous plating. The most important of these is the ease of control since there is no need to provide exact pH adjustment to avoid premature precipitation in the plating bath prior to introduction of the catalytically active surface or to worry about complexing the metal salt to avoid precipitation of metal hydroxides. Another important advantage of the nonaqueous electroless plating is the degreasing capability inherent in the solvent power of the baths themselves which guarantees grease-free surfaces for greater metal adherence.

The process is conveniently conducted at ambient temperature and pressure. The metal salt is typically a halide such as a chloride, bromide or iodide. Various processing conditions are preferred with respect to each individual metal. With respect to chromium, the preferred salt is either chromous chloride or chromic chloride. A preferred bath composition contains one milliliter of a tetrahydrofuran saturated solution of chromic chloride (125 mg./ml.) and two milliliters of a lithium borohydride/ethyl ether solution (10 mg./ml.). Chromous ion (Cr^{+2}) is formed in solution (green color) upon mixing. A second preferred bath composition contains chromous chloride and lithium borohydride, both dissolved in diethylene glycol dimethyl ether. These baths are stable in the absence of a catalytic surface (no change in color; no precipitate or deposit on the walls of the bath) for at least two weeks to one month at ambient temperature. The reducing agent of choice is lithium borohydride and the preferred solvents are the aliphatic ethers such as tetrahydrofuran/ethyl ether (salt solvent/reducing agent solvent) or diethylene glycol dimethyl ether. Molar ratios of chromium salt to reducing agent of 1:2 to 1:50 can conveniently be employed. However, molar ratios of 1 to 1 are preferred. Platings containing from 50 to 75 percent chromium have been obtained. Other useful solvent and reducing agent combinations are illustrated in the table below:

CrCl ₂ /Solvent	Reducing Agent:		Molar Ratio	
	Solvent		CrCl ₂ : Reducing Agent	
Diglyme ¹	LiBH ₄ :	Diglyme	1:6 to	1:12
Diglyme	HCHO:	Monoglyme ²	1:7 to	1:37
Diglyme	NaBH ₄ :	Monoglyme	1:3 to	1:10
Diglyme	KBH ₄ :	Monoglyme	1:2	
Pyridine	NaBH ₄ :	Pyridine	1:3	
Pyridine	N ₂ H ₄ :	Pyridine	1:50	
Pyridine	C ₆ H ₁₂ O ₆ :	Pyridine	1:2 to	1:9
Pyridine	LiBH ₄ :	Monoglyme	1:40	
Pyridine	LiBH ₄ :	Ethyl Ether	1:10	

¹Diethylene glycol dimethyl ether

³Ethylene glycol dimethyl ether

Aluminum trichloride can be employed as an additive in the chromium plating baths wherein it serves to catalyze (i.e., in the presence of the metal surface, the deposition of the metal to be plated is faster in the presence of aluminum trichloride than in its absence) the deposition of the metal to be plated; however, bath stability may be decreased.

With respect to cadmium, an illustrative bath composition contains cadmium diiodide dissolved in tetrahydrofuran and lithium borohydride dissolved in ethyl ether. A preferred molar ratio of cadmium diiodide to lithium borohydride for this bath is 1:2 to 1:4.

With respect to copper, an illustrative bath composition contains cuprous chloride dissolved in tetrahydrofuran and lithium borohydride dissolved in ethyl ether. A preferred molar ratio of cuprous chloride to lithium borohydride for this bath is 1:4 to 1:5. A small amount of aluminum trichloride increases bath stability and helps maintain the bath stable over the plating period.

The following nonlimitive examples illustrate the invention:

EXAMPLE 1

A saturated solution of chromous chloride in pyridine (3.1 mg./ml.; 0.0252 mmole/ml.) was prepared by dissolving anhydrous chromous chloride in dry, freshly distilled pyridine under a nitrogen atmosphere (dry box). A pyridine solution of hydrazine (1.25 mmole/ml.) was prepared in the same manner. The concentrations of the individual solutions were determined by stripping of the solvent in vacuo from a small known volume of solution and weighing the residue.

Tests were conducted under a dry nitrogen atmosphere in small glass vials at ambient temperature. Two milliliters of the hydrazine solution was added dropwise to 2 milliliters of stirred chromous chloride solution by means of a small pipette. A nickel strip which was prepared for plating by degreasing, abrading with emery paper, washing with detergent, rinsing, pickling in hydrochloric acid, rinsing again and drying was placed in the plating bath at the conclusion of mixing. The vials were then capped and the baths allowed to stand at ambient temperature for 18 hours. A heavy dark gray deposit on the nickel strip was scraped off using a stainless steel spatula. Weighed samples of the scraped-off material were dissolved in a phosphoric acid/sulfuric acid mixture made up to a known volume with water and analyzed to be chromium on the Atomic Absorption Spectrometer (ASS).

EXAMPLE 2

The procedure of Example 1 was followed with the exception that 4 milliliters of a pyridine solution of glucose (0.11 mmole/ml.) was used in place of hydrazine solution. A coating was deposited on the nickel strip which was found to be chromium by ASS.

EXAMPLE 3

Following the procedure of Example 1, a plating bath was prepared by adding 0.3 milliliters of an ethyl ether solution of lithium borohydride (25 mg./ml., 1.5 mmole/ml.) to 3 milliliters of a tetrahydrofuran solution of cadmium diiodide (25 mg./ml., 0.068 mmole/ml.) and a nickel strip was placed in the plating bath at the conclusion of the mixing. A coating was deposited on the nickel strip which was found to be cadmium by AAS.

EXAMPLE 4

Following the procedure of Example 1, a plating bath was prepared by adding 0.2 milliliters of an ethyl solution of lithium borohydride (25 mg./ml., 1.5 mmole/ml.) to 3 milliliters of a tetrahydrofuran solution of cuprous chloride (3 mg./ml., 0.022 mmole/ml.) and a nickel strip was placed in the plating bath at the conclusion of the mixing. A coating was deposited on the nickel strip which was found to be copper by ASS.

EXAMPLE 5

The procedure of Example 4 was followed with the exception that a steel strip was used in place of nickel strip. A coating was deposited on the steel strip which was found to be copper by ASS.

We claim:

1. A process for the electroless plating of a metal selected from the group consisting of chromium, cadmium and copper, comprising contacting a salt of said metal dissolved in a nonaqueous organic solvent selected from the group consisting of an alkylene ether and a heterocyclic amine having a monocyclic 6-membered ring containing one hetero-N-atom with a surface which will catalyze the reduction of said salt to the free metal in the presence of a reducing agent for said salt selected from the group consisting of boron compounds which carry at least one hydrogen atom at the boron atom, formaldehyde, hydrazine and reducing sugars to thereby reduce said salt and plate said surface with said free metal.

2. The process of claim 1 in which the reducing agent is dissolved in a nonaqueous organic solvent selected from the group consisting of an alkylene ether and a heterocyclic amine having a monocyclic 6-membered ring containing one hetero-N-atom.

3. The process of claim 1 in which the organic solvent is a solvent for the reducing agent.

4. The process of claim 1 in which the organic solvent is an alkylene ether selected from the group consisting of lower alkylene glycol lower alkyl ethers and monocyclic lower alkylene ethers.

5. The process of claim 1 in which the organic solvent is pyridine.

6. The process of claim 3 in which the reducing agent is a boron compound selected from the group consisting of borohydrides and amine boranes.

7. The process of claim 1 in which the reducing agent is a boron compound selected from the group consisting of alkali metal borohydrides and lower alkoxy substituted borohydrides.

8. The process of claim 1 in which the metal is chromium, the salt is selected from the group consisting of chromous chloride and chromic chloride, the organic solvent is selected from the group consisting of ethyl ether, tetrahydrofuran and diethylene glycol dimethyl ether, the reducing agent is selected from the group consisting of lithium borohydride, sodium borohydride and potassium borohydride and the molar ratio of salt to reducing agent is 1:2 to 1:50.

9. The process of claim 1 in which the metal is cadmium, the salt is cadmium iodide, the reducing agent is lithium borohydride, the organic solvent is selected from the group consisting of tetrahydrofuran and ethyl ether and the molar ratio of cadmium iodide to lithium borohydride is 1:2 to 1:4.

10. The process of claim 1 wherein the metal is copper, the salt is cuprous chloride, the organic solvent is selected from the group consisting of tetrahydrofuran and ethyl ether, the reducing agent is lithium borohydride and the molar ratio of cuprous chloride to lithium borohydride is 1:4 to 1:5.

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