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ELECTROLESS PLATING SYSTEM

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This invention relates to electroless plating wherein metal is plated on a nonconductive surface and, more particularly, relates to the employment of Werner-type chromium complexes to sensitize a surface for such plating.

In the past a number of electroless plating methods have been proposed, but such methods have always required extensive pretreatments such as sealing, sandblasting, etching, and the like, to enhance the chemical bond between the metallic substance and the nonmetallic substrate. These methods have required special machinery and long processing times and have thus increased the cost of such plating.

According to the present invention, these extensive pretreatments are eliminated by employment of Werner-type chromium complexes which are polymerized on the nonconductive surface and which are reactive toward the usual sensitizers and activators used in electroless plating. By Werner-type chromium complexes is meant those compounds wherein a trivalent nuclear atom of chromium is coordinated with a carboxylic acid group to form a cyclic complex. Suitable Werner-type complexes for use in the present invention therefore have a trivalent nuclear chromium atom with an organic acid group complexed therewith. In accordance with the present invention suitable complexes include methacrylate chromic chloride, acrylate chromic chloride, resorcyrate chromic chloride, benzate chromic chloride, palmitate chromic chloride, stearate chromic chloride, and the like. The acid radical may be substituted with other groups, such as alkyl radicals, oxyalkyl radicals, amino radicals, and the like.

In carrying out the present invention, the nonconducting surface to be plated is first coated with a solution of a chromium complex and the complex polymerized. The complex may be an aqueous solution or it can be an organic solvent, such as methanol, propanol, acetone, isopropanol, butanol, and mixtures thereof. Concentration of the chromium complex in the solvent can vary within wide limits and it has been found that solutions containing 1-50% of solids are useful in carrying out the present invention. The chromium complex may be applied by dipping, coating, spraying, brushing, or similar treatment. After the article to be plated is wet with the chromium complex, the complex is polymerized either by drying the complex or by increasing the pH or both. Generally it is preferred to increase the pH, although with some materials increasing the pH would destroy the substrate in which case drying alone would be used. Suitably, the pH of the diluted chromium complex is raised to about 3 to 5 with the addition of a base, such as ammonia, pyridine, hexamethylene tetramine, morpholine, trimethylamine, piperidine, sodium hydroxide, or even with weak acid salts, such as sodium carbonate, or sodium formate.

Drying of the complex can be accomplished by any suitable means, such as ordinary air drying at normal room temperature, oven or hot air drying at temperatures of from 40 to 150° C., infrared drying, induction heating or the like. After drying, a further washing of the treated surface with water, followed by a second drying is frequently employed to increase the effectiveness of the complex. After treatment with the chromium complex, the substrate is treated with a sensitizer, and then with an activator, and is then placed in an electroless plating solution which contains a salt of a desired metal to be plated to-

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gether with a reducing agent, such as a sugar or formaldehyde, or the like. Suitable sensitizers are materials which are readily oxidized and are well known to those skilled in the art, and the particular sensitizer chosen will depend upon the metal to be deposited and the electroless solution. Typical sensitizers include SnCl_2 , $\text{Sn}(\text{BF}_4)_2$, TiCl_3 , AgNO_3 , hydroquinone and HBF_4 to which may be added HCl , NaOH , NaCl , H_2SO_4 , NH_4OH , and the like. Suitable activators are also well known in the art and are salts of the noble metals such as platinum, palladium, gold and silver.

Substantially any nonconducting surface may be plated with the process of the present invention, including ceramics, vitreous masses, glass, cellulose in such forms as wood, paper, cotton, rayon and cellulose acetate, synthetic high molecular weight polymers, wool, silk, proteinaceous materials, such as gelatin coatings, leather, and the like.

It will be understood that the invention is one of broad applicability and that the following examples are for purposes of illustration only.

Example 1.—Two strips of Du Pont Leader film (polyester) were coated by dipping in solutions of beta-resorcyrate chromic chloride supplied by E. I. du Pont de Nemours & Co. The solution as supplied had a solids content of about 3% and a pH of 1. The solvent was isopropanol.

In one solution the pH of the chromium complex was raised to 4 by the addition, under agitation, of a 1% aqueous ammonium hydroxide solution.

In the other, the pH was kept at the original value but was diluted with water at the ratio 1:3.

The samples were dried in an air circulating oven for 3 minutes at 60°-65° C., washed with water, dried again and immersed in a stannous chloride sensitizer solution for 3 minutes and washed with water. The stannous chloride solution had the following composition:

$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$	g	2.3
HCl (36%-38%)	cc	10
H_2O	cc	250

Next the strips were immersed in a palladium chloride activator solution containing:

PdCl_4	g	1
HCl (36%-38%)	cc	10
H_2O	cc	1000

for 2 minutes, washed with water and immersed in the following solution of nickel:

Glycolic acid (Technical 70%)	g	61
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	g	15
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	g	30
NaOH	to bring the pH of the solution to 6	
H_2O	q.s.	1 liter

and maintained at 85° C.

Sound, uniform metallic nickel started to deposit in 5 minutes on both samples.

Example 2.—A strip of cellulose acetate motion picture film was coated with a stock solution of beta-resorcyrate chromic chloride, processed by drying, sensitizing and activating as in Example 1 and immersed in the following electroless copper solution:

$\text{NaKC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	gr	170
NaOH	gr	50
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	gr	35
Aerosol OT 75% Aq (Dioctyl sodium sulfosuccinate)	percent	.005
H_2O	qs.	1 liter.

One part of this solution was diluted with 1 part of water: for every 20 cc. of copper solution, 1 cc. of a

37% solution of formaldehyde was added as a reducing agent.

Sound metallic copper started to deposit in five minutes.

Example 3.—Two strips of a Teflon (polytetrafluoroethylene) film were coated, one with a solution of beta-resorcylochromic chloride as in Example 1 and the other with a stock solution of p-amino benzoato chromic chloride. The latter was supplied as a 3.15% solids solution in isopropanol with a pH of 0.8.

Both samples were dried at 90–110° C. for 3 minutes, washed, dried, immersed in stannous chloride and palladium chloride solutions as indicated in Example 1, washed and immersed in the nickel solution of the same example at the same temperature. After 15 minutes, sound, uniform metallic nickel started to appear on both samples.

Example 4.—A strip of cellulose acetate film was coated with a stock solution of 3,4,5 trimethoxy benzoato chromic chloride in a water-ethanol solvent. The solution contained 1.3% solids and had a pH of 1.2. The sample was treated with the same process and in the same baths as is described in Example 1 and uniform, sound, metallic nickel started to deposit in 5 minutes.

Example 5.—A strip of cellulose acetate film was coated with a stock solution of beta-resorcylochromic chloride, processed as in Example 1 and immersed in an electroless copper solution as follows:

NaKC ₄ H ₄ O:4H ₂ O	-----g--	170
NaOH	-----g--	50
CuSO ₄ .H ₂ O	-----g--	35
AEROSOL OT 75% Aq.	-----percent--	.005
H ₂ O	-----qs.	1 liter.

and mixed in the ratio of 20 to 1 with a 37% solution of formaldehyde. Sound, metallic copper started to deposit in 5 minutes.

Example 6.—Two strips of polyethylene film were coated with a solution of beta-resorcylochromic chloride. One sample was heated for 10 minutes at 80–90° C. in an air circulating oven. The other was heated at the same temperature for 3 days. Both were washed, dried, in the same manner, sensitized with the stannous chloride solution and a palladium chloride solution of Example 1 and then immersed in the copper solution of Example 5. Uniform, sound metallic copper started to deposit in 5 minutes.

Example 7.—Two strips of a Teflon film were coated, one with a solution of beta-resorcylochromic chloride and the other with a stock solution of p-amino benzoato chromic chloride. Both samples were dried at 90–110° C. for 3 minutes, washed, again dried, and then immersed in stannous chloride and palladium chloride solutions as indicated in Example 1. The strips were washed and immersed in the nickel solution of Example 1 at the same temperature. After 15 minutes, sound, uniform metallic nickel started to appear on both samples.

Example 8.—Two Vector Boards (phenolic plastic) were coated with a stock solution of beta-resorcylochromic chloride. The samples were dried for ½ hour at 110° C., washed, again dried, and then immersed in the stannous chloride and palladium chloride solutions of Example 1. They were then washed and immersed, one in the nickel solution of Example 1, the other in the copper solution of Example 5. Sound, metallic, uniform nickel and copper were obtained on the respective boards.

Example 9.—Two phenolic printed circuit boards were coated and treated as the Vector Board of Example 8. The same result was obtained.

Example 10.—The proteinaceous part (i.e. emulsion) of two KODAK Aerographic safety film strips were coated with a stock solution of beta-resorcylochromic chloride. One sample was dried at 60–65° C. for 5 minutes. The other was dried at room temperature. The samples were then washed in water and dried. The sample dried at 60–65° C. was immersed in the stannous chloride and palladium chloride solutions of Example 1. The other was immersed in only the palladium chloride

solution of Example 1. The strips were next washed and immersed in the copper solution of Example 5. Sound, metallic uniform copper was obtained on both samples.

Example 11.—A strip of cellulose acetate was coated with the beta-resorcylochromic chloride stock solution of Example 1. The strip was dried in an air-forced oven at 60–65° C. for 5 minutes, washed, dried, and then immersed in the palladium chloride of Example 1 for 5 minutes. After washing, the strip was immersed in the nickel bath of Example 1. Sound, metallic uniform nickel started to deposit in 15 minutes.

Example 12.—A strip of cellulose acetate was coated with a stearic acid chromium chloride complex solution diluted with 50% water. The sample was dried for 3 minutes at 110° C., washed, again dried at the same temperature, and immersed in the palladium chloride solution of Example 1. The strip was then washed and immersed in the copper solution of Example 5. A copper film having a resistance of 1.5 ohms per square was obtained in 20 minutes.

Example 13.—The Nylon (polyester) portion of a probe holder was coated with a stock solution of 3,4,5-trimethoxy benzoato chromic chloride at pH ca. 4 in a water-methanol. The sample was dried for 3 minutes at 110° C., washed, dried, immersed in the stannous chloride solution of Example 1, washed, and then immersed in the palladium chloride solution of the same example. The sample was then washed and immersed in the nickel solution of Example 1. Sound, metallic, uniform nickel started to deposit in 20 minutes.

Example 14.—Another Nylon holder was coated with a stock solution of beta-resorcylochromic chloride. The sample was dried for 10 minutes at 120° C., washed, dried, and then immersed in the palladium solution of Example 1. The sample was then washed and immersed in the nickel solution of the same example. Sound, metallic, uniform nickel started to deposit in 20 minutes.

Example 15.—A stock solution of p-amino benzoato chromic chloride was diluted with water in the ratio of 1:1 in which 0.05% a Aerosol OT 75% Aq. was dissolved. A strip of a Teflon film was coated with this solution, dried for 10 minutes at 110° C., washed, dried again and immersed in the palladium chloride solution of Example 1 for 5 minutes. The sample was then washed and immersed in the copper solution of Example 5. A copper film with a resistance of 1.2 ohms per square was obtained in 20 minutes.

Example 16.—A strip of safety motion picture film was coated with a 4% solution of p-amino benzoato chromic chloride in isopropanol having a pH of 1. The sample was dried at 110° C. for 3 minutes, washed, dried again at the same temperature and immersed in the palladium chloride solution of Example 1. The sample was then washed and immersed in the following nickel bath:

Nickel hypophosphite	-----g--	26.7
Boric acid	-----g--	1.2
Ammonium sulfate	-----g--	2.6
Sodium acetate	-----g--	4.9
pH	-----	5.5–6.0
Water q.s.	-----	1 liter.

It was found that at 21° C. the deposition of Ni on the sample was very slow and a very good nickel film was obtained in 20 minutes when the nickel bath temperature was increased to 40–60° C.

Example 17.—A strip of cellulose acetate safety film was coated with Quilon C (a stearic acid-chromium chloride complex) stock solution which had been diluted with an equal part of water and the pH raised to 3 with a dilute solution of hexamethylene tetraamine in water. The sample was dried for 3 minutes at 90° C., washed, dried again, immersed in the palladium chloride solution of Example 1 for 3 minutes and in the nickel bath of the same sample. Sound, metallic nickel was deposited in 15 minutes over this sample. Other metallic nickel was de-

posited over the sample by electroplating nickel solution.

Example 18.—A strip of polyethylene film was coated with the same solution of Quilon C used in Example 17. The sample was dried at 110° C. for 5 minutes, washed, dried immersed in the stannous chloride solution of Example 1 for 3 minutes, washed, immersed in the palladium chloride solution of the same sample for 5 minutes. Subsequently, the sample was washed and immersed in the nickel bath, described under Example 15, kept at 40° C. for 15 minutes. Metallic nickel was deposited.

Example 19.—A piece of Plexiglas (polymethylmethacrylate) was coated with a stock solution of p-amino benzoato chromic chloride as in Example 16. The sample was dried at 70° C. for 10 minutes, washed, dried again, immersed in the palladium chloride solution of Example 1 for 5 minutes and washed. Next, the sample was immersed in the nickel bath described in Example 16, kept at 40° C. and metallic nickel started to deposit in 10 minutes. Coating the Plexiglas sheet with a stock solution of p-nitro benzoato chromic chloride or 3,4,5-trimethoxy benzoato chromic chloride and treating it as the sample previously described, the same result is obtained.

Example 20.—A piece of Pyrex glass and a piece of lime glass were coated with a solution of "VOLAN" (methacrylate chromic chloride) supplied by E. I. du Pont de Nemours & Co. The stock solution was diluted with water at a ratio of 1 to 3 and the pH of the resulting solution was raised to 5 by the addition, under strong agitation, of a 1% morpholine solution in water. The samples were dried for 20 minutes at 90° C., washed and dried again. Next, they were immersed in the stannous chloride solution of Example 1 for 2 minutes, washed with water, immersed in the palladium solution of the same example for 3 minutes, washed with water again and immersed in the nickel bath of Example 16 kept at 40° C. Metallic nickel started to deposit in 15 minutes and a very good nickel union was obtained.

Example 21.—20 cc. of a stock solution of Quilon C as supplied by E. I. du Pont de Nemours & Co., was diluted with an equal amount of water. A strip of paper was immersed in this solution and dried at 80° C. Next, the sample was washed with water and dried again. A hydrophobic coating on the surface of the treated paper results. This strip of paper was, subsequently, immersed for 3 minutes in a palladium chloride solution, washed, immersed in the copper solution indicated in Example 5. A deposition of metallic copper film with a resistance of 0.7 ohms per square was obtained in 10 minutes.

Example 22.—A strip of white organdy (cotton fiber) was immersed in the same Quilon C solution and treated with the same process. After palladium chloride sensitization, the sample was immersed in the copper solution described in Example 5. Sound, metallic copper was deposited on each thread of the textile in 15 minutes.

Example 23.—A piece of white nylon (polyester) cloth was immersed in a p-amino benzoato chromic chloride stock solution that was diluted with equal parts of water. The sample was dried at 110° C. for 5 minutes, washed, dried again and immersed in the palladium chloride solution of Example 1 for 3 minutes. With the immersion in the copper bath described in Example 5 a deposition of sound, metallic copper on each thread was obtained in 29 minutes.

Example 24.—A piece of Teflon tape was immersed in a solution of p-amino benzoato chromic chloride stock solution that was diluted with equal parts of water. The sample was dried at 130° C. for 10 minutes, washed, dried again and immersed in the palladium chloride solution of Example 1 for 3 minutes. With the immersion in the copper bath described in Example 5, a deposition of sound, metallic copper was obtained in 30 minutes.

Example 25.—One hundred volumes of styrene monomer 12-T (Dow Chemical Co.) was washed with 25 volumes of 20% aqueous sodium hydroxide. After several washings with vigorous agitation, the monomer was

washed with distilled water until no more caustic was obtained in the wash water and, next, dried over anhydrous calcium sulfate for several hours at room temperature. The monomer was next bulk polymerized by heating it in a closed glass vessel for 160 hours at 130° C. The polymer was dissolved in tetrahydrofuran, dried, dissolved as follows:

	Percent
Xylene	42.5
Toluene	7.5
Methyl ethyl ketone	10
Methyl n-propyl ketone	10
Polymer	30

a film was formed by evaporating the solvent from a thin layer of this material. The thus formed film was coated by dipping in a stock solution of p-amino benzoato chromic chloride diluted with water in the ratio 1:1, dried in an air circulating oven at 60° C. for 5 minutes, washed and dried again. Subsequently it was immersed in a palladium plating bath as follows:

Palladous amine chloride	g/100 cc	2.12
NH ₄ OH	g	24.5
Hydrazine		0.024
Ethylene diamine tetracetic acid tetrasodium salt	g	0.8
Water	q.s.	100 cc.

At 30° C. a deposit of metallic palladium was obtained in 2½ hours. At 60° C. deposition of metallic palladium was obtained in 40 minutes.

Example 26.—A polystyrene film made as described in Example 25 was immersed in a stock solution of p-nitro benzoato chromic chloride solution, dried in an oven at 60° C. for 3 minutes, washed, dried again and immersed in the following silver solution for 3 minutes:

AgNO ₃	g	45
NH ₄ OH 38%	cc	32
H ₂ O	cc	468

The sample was next washed with water and immersed in the solution of Example 5. Sound, metallic copper deposited in 15 minutes.

Example 27.—Clear films of nitrocellulose were obtained by evaporation of solvent from nitrocellulose solutions so formulated:

	Grains
Hercules N.C. RS 25-30 cps.	20
Butyl acetate	20
Xylene, 42.5%; Toluene, 7.5%; Methyl ethyl ketone, 10%; Methyl n-propyl ketone, 10%; Isopropyl alcohol, 15%; N-butyl alcohol, 15%	90

Clear films were cast, by evaporation of the solvent, from this solution.

Stock solutions of:

p-Nitro benzoato chromic chloride
Beta-resorcyloato chromic chloride
p-Amino benzoato chromic chloride
3,4,5 trimethoxy benzoato chromic chloride
Volan

were diluted with water to 1:1 and the films were immersed in each of these solutions and dried in an air circulating oven at 60° C. for 5 minutes. Next, they were washed with water, dried again and immersed in the palladium chloride solution of Example 1 for 3 minutes. After washing with water, the samples were immersed in the copper bath described in Example 5. A deposition of sound, metallic copper was obtained in 10-15 minutes in each instance.

What is claimed is:

1. In the method of electroless plating wherein a non-conducting substrate is sensitized, activated and plated with a metal in an electroless plating solution, the improvement comprising treating said substrate with a

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Werner-type complex of chromium and polymerizing the same prior to sensitization.

2. The process of claim 1 wherein the complex is dried on the surface of a substrate.

3. The process of claim 1 wherein the Werner complex has a pH of from about 3 to 5.

4. The process of plating a metal on a nonconducting substrate comprising the steps of:

(a) wetting the substrate with a solution of a Werner-type chromium complex

(b) causing said complex to polymerize

(c) treating said substrate with a sensitizer solution, said sensitizer comprising an easily oxidized metal salt

(d) treating said substrate with an activator, said activator being a salt of a noble metal

(e) treating said substrate with an electroless plating solution.

5. The method of claim 1 wherein the Werner complex is beta-resorcylato chromic chloride.

6. The process of claim 1 wherein the Werner-type complex is 3,4,5 trimethoxybenzoato chromic chloride.

7. The process of claim 1 wherein the complex is stearato chromic chloride.

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8. The process of claim 1 wherein the complex is p-amino benzoato chromic chloride.

9. The process of claim 1 wherein the complex is methacrylato chromic chloride.

10. The process of electroless plating comprising the steps of

(a) treating a nonconducting substrate with a solution of a Werner-type chromium complex

(b) drying said chromium complex solution on the surface of said substrate

(c) treating said substrate with a stannous chloride sensitizer

(d) treating said substrate with a palladium chloride activator

(e) immersing said substrate in an electroless plating bath whereby a metal is deposited on the surfaces of the nonconducting substrate.

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RALPH S. KENDALL, *Primary Examiner*.