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CHEMICAL METALLIZING PROCESS

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This invention relates to a chemical metallizing process and more particularly to a method of chemically metallizing a substrate by heating a metal salt/phosphine complex in the presence of the substrate.

Metal-coated articles are presently enjoying wide utility. They are often conveniently obtained by chemical or non-electrolytic methods, starting with a compound of the coating metal and converting it to the metal under controlled conditions. In general, however, the known methods are not entirely satisfactory; they each have one or more disadvantages such as requiring exceedingly high temperatures or preformed organometallic compounds, or are limited to aqueous plating baths or to the use of "active" metal substrates in accordance with the electromotive series, or are otherwise not readily adapted to plating a wide variety of substrates. Of particular interest at the present time is the coating of non-metallic substrates such as plastics.

It is an object of this invention to provide a new chemical plating method utilizing readily available metal salts. Another object is to provide such a method which is not dependent on aqueous plating baths, or the activity of the metal substrate in accordance with the electromotive series. Still another object is to provide such a plating process for metallizing a wide variety of substrates, including non-metal as well as metal substrates. These and other objects will become apparent from the following description of the invention.

It has now been discovered that a wide variety of substrates can be chemically metallized by the process which comprises heating a metal salt/phosphine complex derived from one mole of a non-organometallic salt of a normally solid heavy metal of the Deming Periodic Table and about 1 to 4 moles of a triorgano phosphine in which each organo group is a hydrocarbyl or dihydrocarbylamino radical in the presence of the substrate to be metallized at a temperature of about 25° to 350° C., but below decomposition temperature of the substrate and the heavy metal salt alone, provided that when the substrate is not a heavy metal of the Deming Periodic Table other than the plating metal, the metal salt/phosphine complex is in substantially pure form in direct contact with the substrate. By "metallized" is meant metal-coated or metal-impregnated. By "normally solid" heavy metals is meant heavy metals which are solid at normal ambient temperatures, thereby excluding metals such as Hg and Ga which are liquid at temperatures as low as about 30° C. By "plating metal" is meant the heavy metal of the salt from which the complex is derived. By "substantially pure form" is meant undiluted by any substantial amount of solvent, diluent or carrier. Minor amounts of impurities and additives are readily tolerated.

When the substrate is a normally solid heavy metal of the Deming Periodic Table other than the plating metal, the substrate may be immersed in a bath containing the metal salt/phosphine complex dissolved in an inert solvent and the bath is heated for a time sufficient to provide an adherent coating of the plating metal on the substrate.

When the substrate is not a heavy metal of the Deming Periodic Table other than the plating metal, the metal salt/phosphine complex is heated in substantially pure form in direct contact with the substrate. When direct

contact between the complex in substantially pure form and the substrate is required, it is most conveniently provided by coating the substrate with the complex alone, especially in the case of a liquid complex, or by mixing the complex with a volatile carrier such as a solvent or diluent, coating the substrate with the mixture, evaporating the volatile carrier and heating the coated substrate thereby metallizing the substrate.

Because the metal salt-phosphine complexes are soluble in a wide variety of solvents, metal impregnates as well as coatings can be produced with a wide variety of polymeric substrates that are also soluble in such solvents and can be recovered and reconstituted by solvent evaporation. For impregnating a substrate such as plastic the metal salt/phosphine complex and a soluble polymer are dissolved in a mutual inert volatile solvent, the solvent is evaporated to form an intimate metal salt/phosphine-polymer mixture which is heated to produce the impregnated plastic. A solvent is chosen which softens, swells or dissolves the plastic substrate thereby allowing the plating components to penetrate the surface or to become completely and intimately associated therewith. Solutions of the metal salt/phosphine complex and the substrate polymer can be cast as films, spun into fibers or molded into any desired shape and, with evaporation of the solvent and heating, converted into a metallized product.

Broadly, the method of this invention comprises heating the metal salt/phosphine complex in the presence of the substrate to be metallized at the temperature required to effect the metal salt/phosphine to metal transformation in the particular case. The required temperature, which may be as high as 350° C., but usually is in the range of 25° to 250° C., is significantly lower than that required to decompose the metal salt alone to the free metal.

When the substrate is a normally solid heavy metal of the Deming Periodic Table other than the plating metal, plating temperatures generally range from about 25° to 150° C. When the substrate is other than the specified heavy metals, somewhat higher temperatures in the range of about 100° to 250° C. are generally required. In other words, metal plating with the same metal salt/phosphine complex may require different temperatures depending upon whether or not the substrate is one of the specified heavy metals.

While the exact nature of this phenomenon is not definitely known, it is believed that the specified heavy metals may enter into an exchange reaction with the heavy metal of the complex. Although it is not intended that this invention be limited to any particular theory, these exchange reactions could account for the lower temperatures encountered with heavy metal substrates.

However, these exchange reactions do not follow the normal relationships encountered in the electromotive series of the metals as shown for example by Lange in Handbook of Chemistry, 10th Edition, page 1218, McGraw-Hill Book Co. In accordance with this invention, metals such as aluminum, manganese, zinc, chromium, iron, cobalt, nickel and tin are readily plated on a substrate such as copper, which is lower down in the electromotive series than these plating metals. Such exchange reactions are contrary to the accepted rules of the electromotive series.

It is possible that the presence of the phosphine in the complex may alter the normal forces in the electromotive series. It has been found that by proper selection of the phosphine and solvent, any of the heavy metals can be plated on any other heavy metal at substantially reduced temperatures.

The complexes used in accordance with this invention are derived in part from salts of the normally solid

heavy metals of the Deming Periodic Table. These heavy metals are defined in the Deming Periodic Table as shown by H. G. Deming in Fundamental Chemistry, 2nd edition (1947), page 255, John Wiley & Sons, Inc. and by Lange in Handbook of Chemistry, 10th Edition, pages 56 and 57. Suitable heavy metals which may be used in accordance with this invention include: Cu, Ag and Au (Group I–B); Zn and Cd (Group II–B); Al, Tl and In (Group III); Sn, Pb, Ti and Zr (Group IV); Sb, V, Nb, Ta and Bi (Group V); Cr, Mo and W (Group VI); Mn and Re (Group VII); Fe, Ru, Co, Rh, Ni, Pd, Pt, Os and Ir (Group VIII).

The heavy metal salts from which the metal salt/phosphine complexes are derived are non-organometallic salts. By "non-organometallic salt" is meant a salt which is free of carbon-metal bonds. In other words, this invention is directed to the utilization of heavy metal compounds in their commonly available essentially organic salt forms and does not require that the metal salts first be activated by conversion to an intermediary organometallic form. The heavy metals are commonly available and conveniently used as the chlorides, bromides, iodides, cyanides, nitrites, nitrates, perchlorates, fluoroborates, carbonates or carboxylates such as acetates and trifluoroacetates.

Preferred plating metals are the ductile, noble and precious metals of Groups I–B, and VIII, especially the salts of silver, copper, gold, nickel, cobalt, palladium and platinum. Still other preferred plating metals are titanium, chromium, zinc and tin. These are preferably employed as the readily available chlorides, bromides and iodides, but sometimes, as in the case of silver, are more advantageously used as the nitrites, nitrates or perchlorates.

The complexes are also derived in part from triorgano phospines in which each organo group is a hydrocarbyl or dihydrocarbylamino radical. Each of the hydrocarbyl groups, including those in the dihydrocarbylamino radical, may be aliphatic, cycloaliphatic or aromatic and, for reasons of availability and economy, normally contain from about 1 to 10 carbon atoms, but may contain up to about 18 carbon atoms. These groups may be straight-chain, branched-chain, saturated or unsaturated including ethylenic and acetylenic unsaturation. Exemplifying such groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, amyl, hexyl, octyl, decyl, dodecyl, hexadecyl, octadecyl, propenyl, allyl, butenyl, propargyl, octadecenyl, cyclopentyl, cyclohexyl, cyclohexenyl, phenyl, tolyl, xylyl, ethylphenyl, styryl and dodecylphenyl. The trialkyl phosphines are preferred, particularly the trilower alkyl phosphines having from about 1 to 5 carbon atoms in each alkyl group.

The hydrocarbyl secondary amino groups are preferably, for reasons of availability and economy, di-lower alkylamino groups where each alkyl has from about 1 to 5 carbon atoms such as dimethylamino, diethylamino, methylethylamino, dibutylamino, methyl amylamino and diamylamino. Suitable homologs and analogs include dioctylamino, methyl octadecylamino, ethyloctadecenylamino, methyl cyclopentylamino, methyl cyclohexylamino, octyl cyclohexylamino, dicyclohexylamino, N-methylanilino, N-ethylanilino and N-methyl toluidino. The hydrocarbyl group may also constitute a single divalent radical such as the pyrrolidino and piperidino radicals.

The process of this invention may be carried out using a preformed metal salt/phosphine complex, or the complex may be prepared in situ by adding the metal salt and phosphine separately to a solvent in which the complex is soluble. In either case, the complex is formed and acts as a necessary component in the process. When the complex is formed in situ small excesses of metal salt or phosphine may be present. These do not interfere with the metallization process.

As is well known in the art, phosphines and heavy metal salts generally form definite coordination complexes involving from 1 to 4 moles of the phosphine per mole of the salt. For efficient utilization of the heavy metal salt in forming the complex in situ, the phosphine is normally present in amounts corresponding to at least about one mole per mole of heavy metal salt. More than about four moles of the phosphine per mole of salt is generally not needed, but may be used, if desired. The optimum amount of the phosphine may vary depending on the particular heavy metal salt and the substrate to be coated. Usually, however, only about two moles of the phosphine are needed per mole of salt and sometimes only about one, particularly in the case of Group I–B metals. The formation of definite metal salt/phosphine complexes constitutes an important practical advantage since the complexes are easily obtained pure and can be conveniently stored and handled at ordinary temperatures.

In general the metal salt/phosphine complexes decompose to form metal at or slightly above their melting points and in general this is completed at temperatures below about 350° C. As a class, the triaryl phosphine complexes are thermally more stable than the trialkyl phosphine complexes and require higher metallization temperatures. This may be advantageously used where enhanced thermal stability of a complex is needed as in controlled and step-wise metal deposition. Thus, the wide variety of phosphines that are available enables one to control or vary the temperature of metallization to suit the particular processing need.

The metal salt/phosphine complexes, in contrast to the metal salts from which they are derived, are highly soluble in a wide variety of organic solvents making possible the formulation of a wide range of plating compositions. The solvent of course should be substantially inert to the plating ingredients and the substrate. Suitable solvents include alcohols such as methanol, ethanol, 2-propanol and 2-methyl-1-propanol; ethers such as diethyl ether, furan, tetrahydrofuran and dioxane; ketones such as acetone and methyl ethyl ketone; hydrocarbons such as pentane, hexane, isooctane, tetradecane, benzene, xylene and toluene; halogenated hydrocarbons such as chloroform, methylene chloride, carbon tetrachloride, chlorobenzene, dichlorobenzene, trichloroethylene, 1,1,2,2 - tetrachloro-1,2-difluoroethane, 1,1,2-trichloro-1,2,2-trifluoroethane, trichlorofluoromethane, chlorotrifluoromethane and mixtures and azeotropes thereof; nitriles such as acetonitrile, butyronitrile and benzonitrile; amines such as triethylamine, tributylamine, pyridine and picoline; amides such as dimethylformamide, dimethylacetamide, hexamethylphosphoramide and hexaethylphosphoramide; and esters such as ethyl acetate, butyl acetate and amyl acetate.

The main function of the solvent is to provide liquid, easily handled compositions which can effectively bring the metal salt/phosphine complex in intimate contact with the substrate to be metallized. The solvent may also serve to transfer heat to the metallizing components and as a vehicle for other ingredients having beneficial effects such as plating promoters and surface conditioners. Volatile solvents are preferred, particularly those which can be evaporated from the metallizing compositions at temperatures at or below the temperature at which metallization occurs.

The method of this invention can be applied to a wide variety of substrates, including metallic and non-metallic materials. The metals may be any of those normally used for decorative, structural or electrical purposes. These are usually the normally solid heavy metals of the Deming Periodic Table and alloys thereof. For practical reasons the substrate metal is generally different from the plating metal except where special effects such as relief are desired. Besides the heavy metals, other metals may also serve as substrates including the rare earths such as cerium and actinides such as uranium. As pointed out

above the substrate metal may be higher or lower than the plating metal in the electromotive series of the metals.

There may also be used as substrates siliceous solids such as glass, "Pyrex" glass, spun glass, and asbestos; carbonaceous materials such as graphite and the various amorphous carbon blacks; refractory materials such as Carborundum, ceramics and cermets; natural and synthetic cellulosic materials such as cotton, hemp, jute, paper, parchment, wood, cellulose acetate, and rayon; proteinous materials such as silk, wool, leather, mohair and fur. Still other important substrates are the synthetic polymeric compositions exemplified by the polyvinyls such as polyacrylonitrile, polyvinyl chloride, polytrifluorochloroethylene, polytetrafluoroethylene, polystyrene, polyethylene, polypropylene, polyvinyl acetate, polyvinylidene fluoride, poly(alkyl methacrylates) and copolymers thereof; polybutadiene, poly(diallyl esters) such as poly(diallyl phthalate); polyamides such as nylon, polyimides, polyesters, polyurethanes, polyacetals, melamine-formaldehyde, urea-formaldehyde, phenol-formaldehyde and epoxies. When the substrate is a polymeric material, the metallization temperature should be below the deformation temperature of the polymer.

The substrate may be particulate, for example powdered, or it may have a continuous surface in the form of a sheet, film, tape, foil, wire, fiber, fabric or foam. It may be a highly surface porous mass which is to be impregnated and coated at the same time such as a porous catalyst support.

As is well known in the plating art, for best results the substrate to be plated should be clean especially with respect to grease and loose scale. Any of the known techniques may be used to prepare the surface to be plated. For example, metal surfaces can be treated as described by Burns and Bradley in Protective Coatings for Metals, 2nd Edition, Chapter 2, Reinhold Publishing Corporation. Plastic surfaces can also be preconditioned according to known techniques. For example, the surface can be mechanically "satinized" as described by Bruner and Baranano in Modern Plastics, December 1961, and in Chemical and Engineering News, Mar. 25, 1963, pages 48 and 49. Or the surfaces may be chemically etched, as in the case of polyfluoroethylene being treated with an alkali metal-amine solution as described in Canadian Patent No. 653,304, or with an alkali metal-aromatic ether solution as described in U.S. Patent No. 2,809,130.

It is often beneficial to condition the surfaces to be plated, especially metal surfaces, with conditioners such as the commonly employed hydrohalic acids including hydrochloric, hydrobromic, hydrofluoric and hydroiodic acids or sulfuric acid, or by treating with a small amount of an inorganic reducing salt such as stannous chloride. Such promoters may be incorporated directly into the metal salt/phosphine plating composition of this invention, if desired. Conveniently this may be done in a carrier solvent, especially alcohols such as methyl, ethyl and propyl alcohols.

As an improvement within the scope of this invention, it has been discovered by other inventors that for many of the metal salt/phosphine complexes, especially those derived from the noble metals, the temperature or time required for metallization in accordance with this invention can be further reduced by sensitizing the metal salt/phosphine complex to subsequent thermal treatment. Sensitization may be accomplished by incorporating into the metal salt/phosphine complex plating composition a thermally dissociable free radical generator such as carbon tetrabromide or an organic peroxide, or by irradiating the complex with ultraviolet light, or exposing it to an electron beam or contacting it with a spark discharge. By these techniques the temperature requirement can be reduced by as much as 100° C. for plating on non-metallic substrates. The sensitizing step is particularly advantageous in the case of heat sensitive substrates such as certain plastics. This improvement allows the use of a wider variety of complexes with these substrates.

The following examples, illustrating the novel method disclosed herein for metallizing a wide variety of substrates, are given without any intention that the invention be limited thereto. In these examples, all parts and percentages are by weight unless otherwise specified; solutions of metal salt/phosphine complexes, where employed, were prepared and used in non-metallic (usually glass) containers; and metals to be plated were in the form of 1 in. x 1 in. x ⅛ in. coupons unless otherwise noted. Preformed metal salt/phosphine complexes, where used, were prepared by known methods. Adherence of the metal coatings to the substrate was measured by the Scotch tape cross-hatch test.

(A) GROUP I–B PLATING

Examples 1 to 15

A gold plating stock solution was prepared by dissolving 1 part of $(CH_3)_3P \cdot AuCl$ in 80 parts of 95% ethanol containing 5 parts of added concentrated hydrochloric acid. Aliquots were used to plate immersed test coupons of various metals by heating at 80° C. for the time indicated in the table below.

TABLE I

Example	Substrate	Time, hours
1	Aluminum	2
2	Antimony	2
3	Bismuth	2
4	Cadmium	2
5	Cobalt	2
6	Copper	2
7	Lead	2
8	Nickel	2
9	Platinum	8
10	Silver	2
11	Stainless steel	1.5
12	Thallium	2
13	Tin	2
14	Tungsten	4

After the plating treatment, the coupons were removed, washed with water, then acetone, and inspected. All had an adherent gold coating.

Examples 16 to 25

The procedure of Examples 1–15 was repeated with a solution containing 1 part of $(CH_3)_3P \cdot AuCl$, 200 parts of methanol and 3 parts of concentrated hydrochloric acid to produce adherent gold plates on various metal substrates at 60° C. and the time indicated in the table below.

TABLE II

Example	Substrate	Time, hours
16	#2 carbon steel	3.5
17	Hastelloy B	5
18	Lead	2
19	400 Monel	2
20	Nickel	2
21	Ni-O-Nel	2
22	309 stainless steel	2
23	405 stainless steel	4
24	410 stainless steel	1
25	430 stainless steel	4

Example 26

Using the procedure described in Examples 1 to 15, a solution containing 1 part of $(CH_3)_3P \cdot AuCl$, 80 parts of 95% ethanol and 1 part of concentrated hydrochloric acid was used to plate 2 parts of 200 mesh powdered copper, by heating at 80° C. for 2 hours. The powdered copper was uniformly gold plated as evidenced by examination under a microscope.

Example 27

The procedure of Example 26 was repeated using 200 mesh powdered nickel as the substrate with the same result.

Example 28

The procedure of Example 26 was repeated using 200

mesh powdered stainless steel as the substrate with the same result.

Example 29

A plating solution containing 1 part of $(CH_3)_3P \cdot AuCl$, 200 parts of ethanol and 3 parts of concentrated hydrochloric acid was prepared. A 316 stainless steel coupon was placed in the solution for 2 hours at boiling. An adherent gold coating was produced on the 316 stainless steel.

Example 30

The procedure of Example 29 was repeated except that 200 parts of 2-propanol were substituted for the ethanol with the same result.

Example 31

The procedure of Example 29 was repeated except that 200 parts of 2-methyl-1-propanol were substituted for the ethanol with the same result.

Example 32

The procedure of Example 29 was repeated except that 200 parts of acetone were substituted for the ethanol with the same result.

Example 33

The procedure of Example 29 was repeated except that 200 parts of chloroform were substituted for the ethanol with the same result.

Examples 34 to 41

Using the procedure of Examples 1 to 15, various gold-plating compositions were used to adherently plate various metallic substrates under the conditions indicated in the table below.

TABLE III

Example	Plating Solution, parts	Temp., ° C.	Time, hrs.	Substrate
34	1 pt. $(CH_3)_3P \cdot AuCl$, 80 pts. 95% ethanol, 3 pts. conc. HBr.	80	1	Bronze.
35	1 pt. $(C_4H_9)P \cdot AuCl$, 250 pts. acetonitrile.	80	6	Copper.
36	1 pt. $(C_6H_5)_3P \cdot AuCl$, 100 pts. dimethylformamide, 20 pts. acetic acid.	100	0.1	Mild steel.
37	1 pt. $(CH_3)_3P \cdot AuI$, 160 pts. methanol, 1 pt. conc. HF.	60	0.5	Niobium.
38	1 pt. $(CH_3)_3P \cdot AuI$, 160 pts. methanol, 1 pt. conc. HF.	60	1	Aluminum.
39	1 pt. $(CH_3)_3P \cdot AuI$, 160 pts. methanol, 1 pt. conc. HF.	60	1.5	Uranium.
40	1 pt. $(CH_3)_3P \cdot AuI$, 160 pts. acetone, 1 pt. conc. HI.	50	1.5	Aluminum.
41	1 pt. $(C_6H_5)_3P \cdot AuI$, 250 pts. 95% ethanol.	80	1	Stainless steel.

Example 42

Silver-plating compositions, prepared by dissolving 1 part of $(CH_3)_3P \cdot AgI$ in 250 parts of 2-propanol, and adding 0.5 part of concentrated hydrochloric acid, produced lustrous, adherent silver plates on brass coupons immersed in the boiling solution for 0.5 hour.

Example 43

The procedure of Example 42 was repeated using 250 parts of triethylamine in place of the 2-propanol with the same result.

Example 44

The procedure of Example 42 was repeated using 250 parts of acetone in place of the 2-propanol with the same result.

Example 45

The procedure of Example 42 was repeated using 250 parts of acetonitrile in place of the 2-propanol with the same result.

Examples 46 to 51

Various silver-plating compositions were used in the procedure of Examples 1 to 15 to produce lustrous adherent silver plates on various substrates under the conditions indicated in the table below.

TABLE IV

Example	Plating Composition, parts	Temp., ° C.	Time, hrs.	Substrate
46	1 pt. $(CH_3)_3P \cdot AgI$, 20 pts. acetone.	50	2.5	Phosphor bronze.
47	1 pt. $(CH_3)_3P \cdot AgI$, 16 pts. acetone.	50	3	Copper (200 mesh) powder.
48	1 pt. $[(C_6H_5)_3P]_2 \cdot AgNO_3$, 16 pts. 95% methanol.	80	1	"Everdur" Cu-Si-Mn alloy.
49	1 pt. $[(C_6H_5)_2CH_3P]_4 \cdot AgNO_3$, 40 pts. acetonitrile.	80	0.2	Copper.
50	1 pt. $(CH_3)_3P \cdot AgNO_2$, 40 pts. acetonitrile.	80	0.2	Do.
51	1 pt. $(C_6H_{11})_3P \cdot AgNO_2$, 125 pts. acetonitrile.	80	0.2	Do.

Examples 52 to 55

Various copper salt/phosphine complexes were used in the procedure of Examples 1 to 15 to produce lustrous, adherent copper plates on various substrates under the conditions indicated in the table below.

TABLE V

Example	Plating Solution, parts	Temp., ° C.	Time, hrs.	Substrate
52	1 pt. $[(C_6H_5)_3P]_2 \cdot CuCl_2$, 100 pts. dimethylformamide, 20 pts. acetic acid.	100	0.3	Mild steel.
53	1 pt. $[(C_4H_9)_3P]_2 \cdot CuCl_2$, 30 pts. methanol, 0.05 pt. conc. HCl.	60	2	Cast iron.
54	1 pt. $[(C_4H_9)_3P]_2 \cdot CuCl_2$, 100 pts. 95% ethanol, 5 pts. conc. HCl.	80	2	Brass.
55	1 pt. $(C_4H_9)_3P \cdot CuOC(O)CH_3$, 100 pts. acetonitrile.	80	3	Gold.

Example 56

The liquid complex, $(C_4H_9)_3P \cdot AuCl$, was spread on a silicon wafer which was then heated on a 180° C. hot plate. Within 5 minutes, the wafer had become coated with an adherent, electrically conductive gold layer. When cooled, the resistance of the wafer was less than 0.5 ohm/cm.^{2}, or less than $\frac{1}{1000}$ of the original resistance.

It will be apparent to those skilled in the solid state electronics art that this process and the gold-coated silicon produced thereby are useful for preparing integrated microcircuits.

Example 57

A 0.1% solution of $(CH_3)_3P \cdot AgNO_2$ in acetone was spread over a 1 in. x 1 in. film of polytetrafluoroethylene whose surface previously had been treated with a sodium-naphthalene-tetrahydrofuran solution essentially as disclosed in U.S. Patent No. 2,809,120. After the acetone had evaporated, the film was placed with the coated side up on a 100° C. hot plate while the coated side was simultaneously heated with a hot air stream from a commercial hair dryer at a somewhat lower temperature. A bright silver coating appeared almost immediately. The silver coating was flexible, adherent, had a resistance of about 10 ohm/cm.^{2}, and could be wiped with a paper towel to a mirror bright finish. Rubbing and compressing the coating with a spatula further improved its luster and conductivity.

Example 58

Example 57 was repeated on a film of "Delrin" polyacetal resin that had previously been "satinized" as described by Bruner and Baranano in Modern Plastics, December 1961. Simply heating on a hot plate at 150° C. for 15 minutes produced a lustrous, flexible, adherent and electrically-conductive silver coating on the film.

Example 59

The procedure of Example 58 was repeated except that an untreated "Zytel" polyamide resin film was used as the substrate with essentially the same result.

Example 60

The procedure of Example 58 was repeated except that an untreated "Mylar" polyester film was used as the substrate with essentially the same result.

Example 61

The procedure of Example 58 was repeated except that an untreated "Kapton" type H polyimide film was used as the substrate with essentially the same result.

Example 62

A solution containing 1 part of $(C_6H_5)_2CH_3P \cdot AgNO_2$, 1 part of a film-forming vinylidene fluoride/tetrafluoroethylene copolymer and 4 parts of acetone was cast as a film on aluminum foil. The acetone was evaporated and the coated piece heated at 180° C. for 5 minutes to develop a flexible, silvery coating which was adherent to the aluminum foil.

Example 63

The procedure of Example 62 was repeated except that a glass plate was used in place of the aluminum foil with the same result. The metal-impregnated coating adhered to the glass.

Example 64

A piece of "Torvex" ceramic honeycomb (4 in. in diameter, 1 in. thick and having a 3/16 in. pore size) was dipped into one liter of a 1% solution of $(CH_3)_3P \cdot AgNO_2$ in acetonitrile, air dried to evaporate the acetonitrile, and subjected to a stream of hot air from a hot air gun at approximately 200° C. to develop a silvery coating. The procedure was repeated eight times to build up a continuous silver coating throughout the porous structure.

Such product, presenting a large silver surface, but with its open honeycomb structure substantially unchanged so that gas flowing through it remains substantially unimpeded, is useful as a silver catalyst in vapor phase reactions.

(B) PLATING WITH GROUP II–B METALS

Examples 65 to 71

Metal coupons to be plated, 1 in. x 1.5 in. x 1/8 in., were immersed in liquid plating compositions, consisting of 1 part of a bis(trialkylphosphine) metal halide diluted with about 2.5 parts of an inert solvent as specified in the table below. The coupons were held in the baths for the times and at the temperatures noted in the table below, removed, rinsed with water and acetone, and inspected.

Yellow metal substrates were chosen for these tests so that the formation of silvery-white metal coatings would be readily apparent on visual inspection. All coatings were adherent.

TABLE VI

Example	Plating Composition	Temp., ° C.	Time, hrs.	Substrate	Result
65	$[(CH_3)_3P]_2 \cdot ZnBr_2$+dimethylformamide.	100	0.5	Copper	Zn coating.
66	$[(C_4H_9)_3P]_2 \cdot Zn(OC(O)CH_3)_2$ plus dimethylformamide.	25	24	Brass	Do.
67	$[((CH_3)_2N)_3P]_2 \cdot ZnCl_2$ plus hexamethylphosphoramide.	100	24	Copper	Heavy Zn coating.
68	$[((CH_3)_2N)_3P]_2 \cdot ZnI_2$ plus hexamethylphosphoramide.	100	24	do	Do.
69	$[(C_4H_9)_3P]_2 \cdot CdCl_2$ plus tetradecane.	150	0.5	do	Lustrous Cd plating.

(C) PLATING WITH GROUP III METALS

Example 70

Aluminum was plated on copper by heating a copper test coupon at 35° C. for 6 hours in a plating solution prepared by adding 20 g. of triphenylphosphine (0.076 mole) in 100 ml. of ether to a filtered solution containing 5 g. of anhydrous $AlCl_3$ (0.038 mole) in 100 ml. of ether and removing the small amount of oil that separated.

Example 71

Thallium was plated on copper by heating a copper test coupon in a solution containing 2.6 g. of $TlOC(O)CH_3$ (0.01 mole) and 4.1 g. of tributylphosphine (0.02 mole) mole) in 50 ml. of acetonitrile for 3 hours at 80° C.

Example 72

Indium was heavily deposited on a gold coupon by heating the gold coupon in a solution containing 2.2 g. of $InCl_3$ (0.01 mole) and 8.1 g. of tributylphosphine (0.04 mole) in 50 ml. of acetonitrile for 3 hours at 80° C.

(D) PLATING WITH GROUP IV METALS

Example 73

A lustrous and adherent tin coating was obtained on copper by heating a copper test coupon for 2 hours at 60° C. in a plating solution prepared by mixing 1 part each of $SnCl_2 \cdot 2H_2O$ and $(C_4H_9)_3P$ in about 10 parts of methanol. The emission spectrum of the coating corresponded to that of metallic tin.

Example 74

The procedure of Example 73 was repeated except that a silver test coupon was used in place of copper with the same result.

Examples 75 to 81

Metal plates were obtained by immersing a substrate in a plating composition and heating for 16 hours under the conditions summarized in the table below. The plating compositions were prepared by mixing approximately 2.2 molar proportions of a phosphine, a molar proportion of a Group IV–B metal salt and optionally about 10 parts of a diluent per part of metal salt. Visual inspection and, where taken, the X-ray fluorescence or emission spectrum of each resulting test piece showed a Group IV–B metallic coating on its surface.

TABLE VII

Example	Salt	R_3P, R=	Solvent	Temp., ° C.	Substrate
75	$TiCl_3$	Butyl	None	100	Copper.
76	$TiCl_3$	do	Tetrahydrofuran	40	Do.
77	$TiCl_3$	do	Acetonitrile	100	Do.
78	$TiCl_3$	do	Dimethylformamide.	100	Stainless steel.
79	TiI_3	Dimethylamino.	Hexaethylphosphoramide.	100	Copper.
80	$ZrCl_4$	Methyl	do	100	Do.
81	$ZrCl_2$	Dimethylamino.	Dimethylformamide.	100	Do.

(E) PLATING WITH GROUP V METALS

Examples 82 to 88

Metal plates were produced on copper test coupons with the plating compositions specified in the table below which were prepared as in Examples 75 to 81. Heating was 16 hours at 100° C. except in the case of Example 88 which was for 12 hours. Plating in Examples 82 to 84 was confirmed by X-ray emission and fluorescence spectra of the coatings.

TABLE VIII

Example	Plating Composition		
	Salt	Phosphine, R_3P, R=	Solvent
82	VCl_3	Methyl	Dimethylformamide.
83	VCl_3	Butyl	Do.
84	VCl_3	Dimethylamino	Do.
85	$TaCl_5$	Butyl	Toluene.
86	$TaCl_5$	Dimethylamino	None.
87	$NbCl_5$	do	Do.
88	$SbCl_3$	do	Hexamethylphosphoramide.

(F) PLATING WITH GROUP VI METALS

Examples 89 to 92

Metal plates were produced on copper test coupons with the plating compositions specified in the table below which were prepared as in Examples 75 to 81. Heating was 16 hours at 100° C. X-ray emission spectroscopy confirmed that the Example 91 plate was chromium.

TABLE IX

Example	Plating Composition		
	Salt	Phosphine, R_3P, R=	Solvent
89	$CrCl_3$	Dimethylamino	Dimethylformamide.
90	$CrCl_3$	do	Do.
91	$CrCl_2$	do	Do.
92	$MoCl_3$	do	None.

(G) PLATING WITH GROUP VII METAL

Example 93

Following the procedure of Examples 75 to 81, a manganese coating, confirmed by X-ray emission spectroscopy, was plated on copper by heating a test coupon in a $[(CH_3)_2]_3P \cdot MnCl_2$ hexamethylphosphoramide solution for 12 hours at 150° C.

(H) PLATING WITH GROUP VIII METALS

Examples 94 to 103

The procedure followed was essentially that described for Examples 75 to 81, except that the plating compositions and conditions were varied as noted in the table below. In Example 94 the coating was confirmed by emission spectroscopy. In Examples 94 to 97, the salt and phosphine were separately added to the solvent; in Examples 98 to 103, the preformed complex $MX_2 \cdot R_3P$ was added directly to the plating solvent. In all cases the coatings were adherent.

TABLE X

Example	Plating Composition			Temp., ° C.	Time, hrs.	Substrate	Result
	Salt	Phosphine R_3P, R=	Solvent				
94	$FeCl_2$	Me_2N	Hexamethylphosphoramide.	150	12	Copper	Fe coat.
95	$CoCl_2$	Butyl	Acetonitrile	80	3	do	Co coat.
96	$RhCl_2$	Me_2N	Hexamethylphosphoramide.	150	12	do	Rh coat.
97	$NiBr_2$	Phenyl	83% acetonitrile, 17% acetic acid.	80	.1	do	Bright Ni coat.
98	$NiCl_2$	Butyl	Acetic acid	100	3.5	do	Lustrous Ni coat.
99	$NiBr_2$	do	do	100	2	Bronze	Do.
100	$NiCl_2$	Methyl	95% ethanol plus 5% conc. HCl.	70	2	Brass	Ni coat.
101	$PdCl_2$	do	do	70	.1	do	Lustrous Pd coat.
102	$PtCl_2$	do	95% ethanol plus trace HF.	70	7	Copper	Lustrous Pt coat.
103	PtI_2	do	do	70	7	do	Pt coat.

Example 104

About 1 g. of finely powdered $[(CH_3)_3P]_2 \cdot PdCl_2$ was spread on a 2 ml thick, 3 in. x 3 in. square of a high temperature resistant "Kapton" type H polyimide film. The coated film was gradually heated on a hot plate under a nitrogen atmosphere to about 350° C. until the complex had decomposed and had deposited on the film an adherent, lustrous, electrically-conductive palladium coating.

Such metallized polyimide structures are particularly useful for preparing mirrors, automotive interior hardware, printed circuits and battery electrodes.

(I) EXAMPLES ILLUSTRATING IMPROVEMENTS WITHIN THE SCOPE OF THIS INVENTION

Example 105

One part of $(CH_3)_3P \cdot AuCl$ was dissolved in 25 parts of a 15% solution of "Orlon" polyacrylonitrile in dimethylformamide. The solution was spread on a glass microscope slide and warmed with a heat lamp to evaporate the dimethylformamide. The slide was then exposed to a Tesla coil spark discharge to sensitize the gold salt complex to thermal decomposition and placed treated-side up on a 200° C. hot plate for about 5 minutes. The resulting uniformly distributed golden coating was adherent to the glass and electrically conductive.

Example 106

A $(CH_3)_3P \cdot AuCl$/polyacrylontrile/dimethylformamide solution, substantially as described in Example 105, was spread on a glass slide and the dimethylformamide evaporated by warming under a heat lamp. The resulting film was then covered with a stencil, irradiated with high intensity light by contact flashing with a 200 watt-second xenon flash tube (Hico lite, Model K; one millisecond duration flash), then heated at 100° C. for about 5 minutes. The resulting slide showed a lustrous, electrically conductive, adherent golden image corresponding to the irradiated areas.

Example 107

Example 105 was repeated with 1 part of

$(CH_3)_3P \cdot AuCl$

per 5 parts of poly[4,4'(hexafluoroisopropylidene)diphenol isophthalate] polyester as the carrier substrate in 100 parts of methylene chloride. The resulting film, after having been exposed to the spark discharge and heated at 200° C. for 2 minutes, was golden, adherent and electrically conductive.

Such products are useful in printed circuitry for use at elevated temperatures.

Example 108

The procedure of Example 107 was repeated except that a piece of porcelain was used in place of the glass slide with substantially the same result.

Example 109

The procedure of Example 107 was repeated except that a piece of wood was used in place of the glass slide with substantially the same result.

Example 110

The procedure of Example 107 was repeated except that a carbon sheet was used in place of the glass slide with substantially the same result.

Example 111

The procedure of Example 107 was repeated except that a piece of ceramic was used in place of the glass slide with substantially the same result.

Example 112

Repeating Example 107 with 0.5 part of the gold complex produced uniformly colored purple slides, indicating colloidal gold dispersed throughout the polymeric film, which were useful as interference filters.

Example 113

A mixture of 1 part of $(CH_3)_3P \cdot AgNO_2$ and 70 parts of film-forming polyvinylchloride, cast as a film on glass from dimethylformamide solution, was irradiated 3 times through a stencil with the light source described in Example 106 and then heated to 180° C. for 5 minutes to develop a silvery image. The silver deposit was much less noticeable in the unirradiated area.

Example 114

The procedure of Example 113 was repeated except that 1 part of $(C_4H_9)_3P \cdot AgClO_4$ was used as the silver complex with the same result.

Example 115

The procedure of Example 113 was repeated except that 1 part of $(C_6H_5)_3P \cdot AgOC(O)CH_3$ was used as the silver complex with the same result.

Example 116

The procedure of Example 113 was repeated except that 1 part of $(C_4H_9)_3P \cdot AgI$ was used as the silver complex with the same result.

Example 117

The procedure of Example 113 was repeated except that 1 part of $(C_6H_5)_3P \cdot AgOC(O)CF_3$ was used as the silver complex with the same result.

Example 118

The procedure of Example 113 was repeated except that 1 part of $[(C_6H_5)_3P]_2 \cdot Ag_2CO_3$ was used as the silver complex with the same result.

Example 119

The procedure of Example 113 was repeated except that 1 part of $(C_4H_9)_3P \cdot AgCN$ was used as the silver complex with the same result.

Example 120

The procedure of Example 113 was repeated except that 1 part of $(C_6H_5)_3P \cdot AgNO_3$ was used as the silver complex with the same result.

Example 121

The procedure of Example 56 was repeated except that a small, catalytic amount of carbon tetrabromide was added to the liquid complex, $(C_4H_9)_3P \cdot AuCl$, before it was spread on the silicon wafer. Decomposition of the complex to form the gold coating was speeded up considerably.

Thus, it should be apparent from the above examples that this invention has wide utility. It is useful to produce metallized objects having continuous, adherent and, where needed, flexible, electrically conductive metal coatings. For example, it is useful to produce (1) metallic coatings that protect the underlying material and that reflect light and infrared radiation; (2) electrically conductive articles such as printed circuits, resistors, capacitors, and electrodes for fuel cells and batteries; (3) various decorative pieces (e.g. automotive hardware); effects, and images based on the formation of metal surfaces; (4) new catalyst structures wherein a catalytically active heavy metal is impregnated and coated on a porous substrate carrier; and (5) metallized films showing selective light transmission which can be used as optical filters. It is also useful to obtain coatings of the normally brittle metals such as titanium, zirconium, chromium, vanadium, niobium, and manganese which are difficult to obtain by other methods. It is also useful to produce metallized plastics wherein the metal is uniformly distributed throughout the body of the plastic as well as on its surface. This is of great practical advantage when the surface of the plastic is normally subjected to abrasion.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of chemically metalizing a substrate which comprises heating a metal salt/phosphine complex derived from one mole of a non-organometallic salt of a normally solid heavy metal of the Deming Periodic Table and 1 to 4 moles of a triorganophosphine in which each organo group is a hydrocarbyl or dihydrocarbylamino radical in the presence of the substrate to be metallized at a temperature of 25° to 350° C., but below the decomposition temperature of the substrate and the metal salt alone, provided that when the substrate is not a heavy metal of the Deming Periodic Table other than the plating metal, the metal salt/phosphine complex is in substantially pure form in direct contact with the substrate.

2. The method of claim **1** in which the substrate is a heavy metal other than the plating metal, the metal salt/phosphine complex is dissolved in an inert solvent and the temperature is 25° to 150° C.

3. The method of claim **2** in which the complex is derived from a salt of a heavy metal of Group I–B or VIII of the Deming Periodic Table and a trialkylphosphine.

4. The method of claim **1** in which the substrate is not a heavy metal other than the plating metal.

5. The method of claim **4** in which a solution containing the metal salt/phosphine complex in a volatile inert solvent is coated on the substrate, the solvent is evaporated, and the coated substrate is heated to metallize the surface.

6. The method of claim **5** in which the complex is derived from a salt of a heavy metal of Group I–B or VIII of the Deming Periodic Table and a trialkylphosphine.

7. The method of claim **5** in which the temperature is 100° to 350° C.

8. The method of claim **6** in which the complex is derived from gold chloride and a tri-lower alkylphosphine and the substrate is a polymeric material.

9. The method of claim **6** in which the complex is derived from silver nitrite and a tri-lower alkylphosphine and the substrate is a polymeric material.

10. The method of claim **6** in which the complex is derived from silver nitrite and a tri-lower alkylphosphine and the substrate is a porous ceramic body.

11. The method of claim **6** in which the complex is derived from palladium chloride and a tri-lower alkylphosphine and the substrate is a polymeric material.

12. The method of claim **4** in which the metal salt/phosphine complex and a soluble polymer are dissolved in a mutual inert volatile solvent, the solvent is evaporated to form an intimate salt/phosphine/polymer mix-

ture, and the mixture is heated to produce a metallized polymeric product.

13. The method of claim **12** in which the complex is derived from a salt of a heavy metal of Group I–B or VIII of the Deming Periodic Table and a trialkylphosphine.

14. The method of claim **13** in which the temperature is 100° to 350° C.

15. The method of claim **13** in which the complex is derived from gold chloride and a tri-lower alkylphosphine.

16. The method of claim **13** in which the complex is derived from silver nitrite and a tri-lower alkylphosphine.

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