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3,672,923

## SOLID PRECIOUS METAL SENSITIZING COMPOSITIONS

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No Drawing. Continuation-in-part of application Ser. No. 9,060, Feb. 5, 1970, which is a continuation-in-part of application Ser. No. 801,167, Feb. 20, 1969, which is a continuation-in-part of application Ser. No. 712,575, Mar. 12, 1968, which is a continuation of application Ser. No. 551,249, May 19, 1966, which is a continuation of application Ser. No. 285,889, June 6, 1963, which in turn is a continuation of application Ser. No. 53,352, Sept. 1, 1960. This application June 29, 1970, Ser. No. 50,918

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18 Claims

### ABSTRACT OF THE DISCLOSURE

Solid compositions dilutable to optically clear sensitizing solutions for rendering surfaces receptive to the deposition of an adherent electroless metal comprise a metal complex consisting of (a) a precious metal selected from a group consisting of the precious metals of the fifth and sixth periods of Groups VIII and I-B of the Periodic Table of Elements, (b) a Group IV metal of the Periodic Table of Elements which is capable of two valence states and (c) an anion capable of forming a stable moiety with both valence states of the Group IV metal, in which the molar ratio of (a) to (b) to (c) is from about 1:1:3 to 1:6:24. The solutions can be prepared by diluting the solid compositions. Controlled excesses of (b) and (c) and hydrogen ion and wetting agents enhance the solubility of the powdered product and stability of the diluted solutions. Processes for rendering surfaces receptive to the deposition of an electroless metal, e.g., copper, nickel, cobalt, palladium, gold and silver, are also provided.

### CROSS-REFERENCES TO RELATED APPLICATIONS

This application is a continuation-in-part of U.S. application, Ser. No. 9,060, filed Feb. 5, 1970, which in turn is a continuation-in-part of U.S. application Ser. No. 801,167, filed Feb. 20, 1969, which in turn is a continuation-in-part of U.S. application, Ser. No. 712,575, filed Mar. 12, 1968, now abandoned, which in turn is a continuation of U.S. application Ser. No. 551,249, filed May 19, 1966, now abandoned, which in turn is a continuation of U.S. application Ser. No. 285,889, filed June 6, 1963, now abandoned, which in turn is a continuation of U.S. application Ser. No. 53,352, filed Sept. 1, 1960, now abandoned.

Generally stated, the subject matter of the present invention relates to new and useful precious metal sensitizing compositions. More particularly, the invention relates to solid compositions comprising a precious metal complex, and to solutions prepared therefrom. The solutions are used to render surfaces of a substrate catalytic to the reception of an electroless metal.

### BACKGROUND OF THE INVENTION

The electroless deposition of a metal on either a metallic substrate usually requires pretreatment or sensitization of the substrate to render it catalytic to the reception of such deposit. Various methods have evolved over the years employing particular sensitizing compositions.

One of the earliest innovations employed a plurality of baths in which the substrate was subjected to a basic two-

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step process entailing immersion in a stannous chloride solution, followed by immersion in an acid palladium chloride solution. More recently, there has been proposed a unitary treating process which employs a colloidal dispersion, i.e., not a clear solution, of palladium and tin. See U.S. Pat. No. 3,011,920, Shipley.

The plural bath process, while readily effecting sensitization, deposits on metals a flash coating of the precious metal from the sensitizing bath. The precious metal so flash coated from the sensitizing bath disrupts the balance of the bath. Thus, to maintain catalytic activity, the addition of the precious metal bearing solution to the bath is required. This, of course, increases the cost of the plural bath process. Furthermore, flash coating of precious metal normally leads to a low grade of adhesion, thereby materially affecting the bond and peel strength of an electroless metal deposit.

The prior unitary bath process on the other hand, while overcoming the problem of flash coating, has a diminished reactivity and requires longer periods of time for sensitization. Moreover, because colloids are involved, dry, stable solids, suitable to prepare such baths by dilution, are not feasible to prepare, ship or store because of destruction of the colloidal dispersion by flocculation when the preparative mixture is concentrated. Unitary bath sensitizers in a dry powder form would be desirable because shipping and storage costs would be minimized; and process solutions are more simply put together (by dilution, for example).

It has now been found possible to provide a solid composition which is practically instantly dilutable into a unitary sensitizing solution with higher activity than can be obtained with prior art baths.

Accordingly, it is a primary object of the present invention to provide a new solid sensitizer composition, and diluted stable solutions thereof, that are highly active, as well as new processes to effect the sensitization of a substrate to render it catalytic to the reception of an electroless metal deposit.

Another object of the present invention is to provide new and useful solid compositions which are dilutable to true solutions and methods for sensitizing substrates using them which substantially obviate the problem of non-adherent precious metal flash coatings.

It is an additional object of the invention to provide solid compositions, dilutable to optically clear sensitizing solutions and processes for the use thereof which materially reduce the time necessary to effect sensitization.

Yet another object of the invention is to provide solid compositions and methods for sensitizing substrates with a precious metal which involve using very dilute treating solutions and thereby materially diminishing production costs.

Additional objects and advantages will be set forth in part in the description which follows, and in part will be obvious from the description, or may be realized by practice of the invention, the objects and advantages being realized and attained by means of the methods, processes, instrumentalities and combinations particularly pointed out in the appended claims.

### DESCRIPTION OF THE INVENTION

To achieve the foregoing objects, and in accordance with its purposes as embodied and broadly described, the present invention relates to solid compositions, dilutable to optically clear, sensitizing solutions for rendering surfaces receptive to the deposition of an adherent electroless metal which comprise a metal complex consisting of three components:

(a) A precious metal selected from the group consisting of the precious metals of the fifth and sixth periods



of Groups VII and I-B of the Periodic Table of Elements;

(b) A Group IV metal of the Periodic Table of Elements which is capable of two valence states; and

(c) An anion capable of forming a stable moiety with both valence states of the Group IV metal, the molar ratio of components (a) to (b) to (c) being from about 1:1:3 to 1:6:24.

The complexes with which the instant invention is concerned are formed reversibly. Therefore, an excess of component (b) appears to enhance their formation. It has been found, however, that too much of an excess of component (b) results in a reduced sensitizing capability. Below a ratio of 3 moles of component (b) for each mole of complex, the complex anion, while formed, is difficult to stabilize. On the other hand, if the amount of component (b) is in excess of about 100 moles per mole of complex, sensitizing activity is noticeably reduced. In practice, a solution containing a relatively large excess of component (b) is preferred for long operating life. Best results are obtained when an excess of component (b) is present in an amount to provide from about 5 to 70 moles of component (b) for each mole of complex in the total composition.

In addition to preferring compositions which contain a relatively large excess of component (b), it is preferred to use a large excess of component (c) to solubilize the complex. In the most preferred embodiments this will be introduced in the form of  $\text{Cl}^-$  or  $\text{Br}^-$  or  $\text{SnCl}_3^-$  and preferably as  $\text{HCl}$ . Extremely large excesses of this component do not seem to be detrimental to sensitizing activity. As to  $\text{HCl}$ , this seems to serve a two-fold purpose: it provides both a large excess of  $\text{Cl}^-$  ion and also  $\text{H}^+$  ions, both assisting in the solubilization of the powdered product. Low pH alone, as produced, for example, by fluoboric acid does not solubilize the powder unless excess component (c) too is present, e.g., sodium chloride can be added. A high excess of component (c), e.g., sodium chloride alone, 25 to 100 moles per mole of complex, helps dissolve the complex and any excess component (b). However, for example, if component (b) is stannous chloride or a similar hydrolyzable composition which forms a basic salt, e.g.,  $\text{Sn}(\text{OH})\text{Cl}$ , unless acid too is present to prevent hydrolysis, an insoluble hydrolysis product is formed which appears to adsorb the composition causing it to be inactive as a sensitizer. Accordingly, in preferred embodiments, to prevent hydrolysis of the Group IV metal, i.e., component (b), acid will be added. High concentrations of acid are preferred, as will be explained hereinafter.

Also contemplated by this invention are optically-clear sensitizing solutions which have been prepared by diluting the solid compositions with an acid or a mixture of water and an acid, until the concentration of component (a) has been reduced to a concentration of from about 0.0003 gram/liter to about 1.5 grams per liter.

Another feature of the invention is a process to prepare the concentrate comprising heating an aqueous mixture of the components (a), (b) and (c) at a temperature of from about  $80^\circ\text{C}$ . to about the boiling point until formation of the complex is complete, and then concentrating the mixture until a friable, solid product is obtained.

Still another feature is a process to prepare the concentrate which comprises mixing an aqueous solution of components (a) and (c) with an aqueous solution of components (b) and (c) and heating the mixture at from  $80^\circ\text{C}$ . to its boiling point, and then concentrating the mixture until a friable, solid product is obtained.

The present invention further relates to an improved process for rendering surfaces receptive to the deposition of an adherent electroless metal, as well as a process for electrolessly depositing a metal on a substrate which has been sensitized with the sensitizing solutions of the present invention.

An additional embodiment of the invention relates to

particular acidic precious metal solutions for rendering surfaces receptive to the deposition of electroless copper, nickel, cobalt, palladium, gold or silver, and especially to copper or nickel.

The invention consists of the novel methods, processes, steps and improvements shown and described.

It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory and are not restrictive of the invention. For example, while copper deposition is described, the teachings are applicable to nickel, palladium, cobalt, silver and gold deposition as well.

Accordingly, the present invention provides a significant improvement over the known sensitization techniques and compositions in that a procedure and composition is provided which will cause conductive and non-conductive materials to be so sensitized simultaneously that efficient and uniform deposition of an adhering electroless metal thereon may be readily effective; thus permitting, by way of illustration, copper plating of the non-metallic surfaces of the side walls of the apertures defined in a plastic base material, as well as the concomitant adherent electroless deposition of copper on pre-formed copper surfaces on the plastic base. Illustrative of the conductive and non-conductive, metallic and non-metallic surfaces which can be plated uniformly with adherent electroless metal by use of the sensitizing solutions and techniques of the present invention are plastic surfaces and surfaces of metallic copper, iron, nickel, cobalt, silver, gold and alloys thereof, such as brass, sterling silver and the like. The present invention can be employed to render a surface catalytic to the reception of such metals as copper, nickel, palladium, cobalt, silver, gold and the like.

A further advantage of the present invention is that sensitization as taught herein leads to practically complete avoidance of the deposition of a flash coating of precious metal from the sensitizing bath. A flash coating of precious metal normally leads to a low grade of adhesion. Also, avoidance of such deposition economically conserves the precious metal.

Yet another advantage of the present invention is realized in manufacturing presensitized plastic base members. In essence, the sensitizing solution can be directly incorporated in a plastic base at the time of its manufacture. This can be achieved by utilizing an organic sensitizing solution employing a solvent such as cyclohexanone, a highly viscous paste like composition. Alternatively, the solution can be reduced to a solid form by employing a counter ion and directly incorporating such solid in a plastic base at the time of manufacture. Therefore, the advent of the present invention provides for the preparation of presensitized plastic substrates.

The most notable advantage occasioned by the advent of the present invention resides in the fact that such solutions possess a sensitizing activity at dilute levels. In essence, a complex is formed between the metals and the anion. The preferred palladium-tin-chloride solid complex of this invention is acid soluble. It is optically clear in dilute solution. It is filterable through ultra-membranes through which colloidal sensitizers will not pass. It has an ultraviolet absorption peak in aqueous acidic solution at  $295\text{--}310\text{ m}\mu$  and  $320\text{ m}\mu$ . Solid compositions comprising the complex according to this invention may be diluted to levels of concentration which can easily and reproducibly be directly formulated into active sensitizing solutions. In other words, the invention makes available stable sensitizing solutions comprising significantly lower concentrations of precious metal than can be produced by other known methods, excluding, of course, the methods of copending applications Ser. No. 9,060, filed Feb. 5, 1970 and Ser. No. 801,167, filed Feb. 20, 1969.

The treating or sensitization procedure which is an embodiment of this invention is an intermediate step between pretreatment or cleaning of the surfaces upon which the metal is to be electrolessly deposited and the actual deposi-



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tion of the metal. The treatment to be afforded the surface to be plated depends upon the cleanliness of the material to be treated and associated factors. Thus, where the surface to be plated is either unclean or its cleanliness uncertain, the first step in the procedure for effecting deposition of adherent electroless metal is to clean thoroughly the article or panel upon which plating is to occur. This is desirably accomplished by scrubbing the panel with pumice or the like to remove heavy soils; rinsing with water; and subsequent removal of soil due to organic substances from the panel and apertures defined therein with a suitable alkali cleaning composition. A typical alkaline cleaner composition is as follows:

	Grams/liter
Sodium isopropyl naphthalene sulfonate -----	3
Sodium sulfate -----	1
Sodium tripolyphosphate -----	14
Sodium metasilicate -----	5
Tetrasodium pyrophosphate -----	27

This operation is desirably performed at a temperature of 160° to 180° F. The surfaces to be plated are permitted to remain in the bath for a period of 5 to 30 minutes. Other suitable alkali cleaning compositions, such as conventional soaps and detergents, may also be used. Care should be used in selecting the detergent to insure that the specimen to be treated is not attacked by the cleaner.

Oxides are removed from copper panel surfaces and apertures by application of a light etching solution such as a 25 percent solution of ammonium persulfate in water as is described in Bulletin No. 86 of the Becco Chemical Division of the Food Machinery and Chemical Corporation, Buffalo, N.Y. The surface oxides also may be removed by application of the cupric chloride etchant solution described by Black in U.S. Pat. No. 2,908,557. This treatment should not exceed 2 to 3 minutes.

The treatment period and temperature are significant, particularly where the panel surfaces are formed of a conductive metal, in that elevated temperatures and extended periods of time beyond those described may result in removal not only of the oxide materials but of the conductive metal, such as copper foil, forming the surfaces of the panel. The panel is rinsed thoroughly after this step with water to remove all semblance of etching compounds. Care should be taken to avoid the formation of further oxide film during rinsing or as a result of air oxidation. Subsequent to rinsing, the panel may be inserted in an acid solution comprising, for example, 10-20 percent by weight of hydrochloric acid in water for a period of from 2 to 5 minutes, and from this bath the panel is placed in the sensitization or treating solution of the present invention.

If the shape of the material permits, a sanding operation with a fine abrasive can also be used to remove oxides.

The sensitizing solution prepared by diluting the solid composition comprises an acidic aqueous solution of a metal complex as defined above consisting of (a) a precious metal, (b) a Group IV metal and (c) an anion. It is optically-clear, i.e. non-colloidal. Among the precious metals that may be employed are palladium, platinum, gold, rhodium, osmium, iridium and mixtures of these metals. The inorganic and organic acid salts of these metals, and of the Group IV metals, such as the chlorides, bromides, fluorides, fluoborates, iodides, nitrates, sulfates and acetates of stannous tin, titanium and germanium among others may be used. Other acid salts of the precious metals and Group IV metals will readily suggest themselves to those skilled in the art. The salts are preferably soluble in water, or in organic or inorganic acid aqueous solutions. Among the salts, the chloride is preferred, both for the precious metal, and the Group IV metal compound. The preferred precious metals and Group IV metal are palladium or platinum, particularly palladium, and stannous tin. In the sensitizing solution bath the precious metal concentration should be from at least about 0.0003 to about 1.5 grams/liter of solution. While the higher end of this

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range causes sensitization to be completed in very abbreviated periods of time, e.g. ten seconds, the lower end of this range is normally more economic. The bath can be prepared directly or by diluting a concentrate.

In one manner of proceeding, the solid composition as defined above are diluted with an aqueous solution of suitable acid. If a dry power acid, e.g., citric acid, is included in the composition, water alone can be used. The solid compositions are prepared by heating the salts of the precious metals and a Group IV metal salt in an aqueous solution of suitable acid as will be described hereinafter and evaporating substantially to dryness. Among the acids that may be mentioned are hydrochloric acid, hydrofluoric acid, sulfuric acid, citric acid, acetic acid and the like. Preferably, the anion of the inorganic acid corresponds to the anion of the salt of the precious metal, or to the anion of the Group IV metal salt. Where the anions of the precious metal salt and the Group IV metal salt are the same, the anion of the acid should preferably correspond to the common anion of the salts. Where the anion of the precious metal differs from that of the Group IV metal salt, the anion of the acid preferably corresponds to the anion of the precious metal salt. However, acids having anions which differ from the anions of the precious metal salts or of the Group IV metal salt may also be used. The hydride anion, H<sup>-</sup>, can be part of the complex. Preferred anions are Cl<sup>-</sup> and SnCl<sub>3</sub><sup>-</sup>.

The concentration of the acid in the sensitizing solutions depends upon the strength of the acid employed. The concentration of the acid should be at least sufficient to prevent hydrolysis of the Group IV metal, at the final concentration. A suitable lower limit is 0.001 normal. At the upper end of the concentration of the acid may be as high as 15 normal, or even higher. When strong acids are used, the concentration of the acid in the sensitizing solution generally varies between about 0.02 and 7.5 normal. When weak acids are used, the concentration of the acid in the sensitizing solution approaches the upper limit given hereinabove. The concentration of acid in the sensitizing solution should, of course, also be high enough to solubilize the salts of the precious metals and the Group IV metal and also be high enough to render the solution suitable for use as a sensitizer for the material being treated. Care should be used in selecting the acid concentration to insure that the specimen being treated is not adversely attacked or corroded by the treating solution.

The Group IV metal ion concentration may vary widely but must be maintained in excess of a stoichiometric amount based on the amount of precious metal ions present in the sensitizing solution. Normally a large excess of, for example, stannous chloride, is maintained to allow for air oxidation of the stannous ion. Illustratively, concentrations of as high as 50 grams per liter of stannous chloride are not detrimental to the effectiveness of the sensitizing activity of the diluted solutions.

The sensitizing solutions of the present invention may contain additional agents to stabilize the solution, e.g., against the effects of atmospheric oxidation. Such agents will include the use of additional quantities of the Group IV metal, as for example, additional stannous chloride may be added to a palladium-stannous chloride sensitizing solution, as well as compounds, such as organic hydroxy compounds (ols), dihydroxy compounds (diols) and polyhydroxy compounds (polyols), the fluorinated hydrocarbon wetting agents and hydrogen fluoride. One result of the addition of such compounds to the sensitizing solution is the inhibition of oxidation of the Group IV metals and the subsequent reduction of the precious metals. The stabilizers, if solid, can be compounded with the solid sensitizer or they can be co-deposited therewith by mixing solutions and evaporating the solvents.

As has been mentioned above, addition of the stabilizing ingredients to the complex is an embodiment of this invention which improves the stability of the solution and avoids formation of undesirable sludges on surfaces, e.g.,



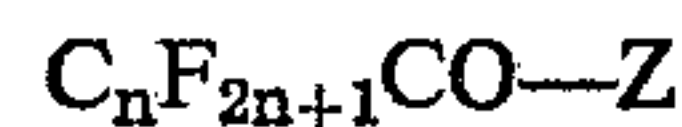
metal surfaces, exposed to such solutions. The nature of the stabilizing ingredient is not particularly critical. It should be soluble at least in an amount great enough to provide the desired stabilization effect. Evidence of effective stabilization is easily observed in comparison with control baths, i.e., those without the stabilizing ingredient present. These latter baths over a period of one week or so will be seen to deposit a film of metallic compound or to precipitate such a compound. On the other hand, baths to which an effective amount of the stabilizing ingredient has been added will remain clear and be stable and storable for periods of at least two weeks and even longer. In any event, the minimum amount will vary somewhat from compound to compound but is easy to determine routinely. There is no apparent reason to limit the quantity of the stabilizing ingredient to the minimum effective amount and often substantially more will be used, the choice being primarily dictated by economic considerations.

The stabilizing ingredient need not be completely water soluble, although for ease of formulation a high degree of water solubility is desirable. As will be obvious to those skilled in the art, the hydroxy compounds which can be used most efficiently would be of relatively low molecular weight, polysubstituted with hydroxy groups or containing at least one hydroxy group and other functional groups such as sulfonic acid groups, phosphate groups, amino groups, halogens, carboxyl groups and the like, which tend to enhance solubility in polar media.

Similar considerations are involved in selecting the most efficient fluorinated hydrocarbon wetting agents. These will be characterized by a stable fluorocarbon tail and a solubilizing group, Z. The solubilizing group can be organic or inorganic, anionic, cationic, nonionic, amphoteric and water soluble. The wetting agents should be active in acidic solutions and have good thermal stability. Especially preferred are those wherein Z is anionic. A preferred species has the following spectrum of solubilities in acid media, in grams/1000 grams of solution: 12½% hydrochloric acid, >1; 37% hydrochloric acid, 0.1; 12½% nitric acid, >1; 70% nitric acid, >5; 12½% phosphoric acid, >1; 85% phosphoric acid, >1; 12½% sulfuric acid, 10; and 97% sulfuric acid, 0.5. Another preferred species has the following solubility spectrum: 12½% hydrochloric acid, <10; 12½% nitric acid, <20; and 12½% sulfuric acid, <10. Particularly useful fluorinated hydrocarbon wetting agents of this type are sold under the trade name Fluorad by the Minnesota Mining and Manufacturing Company, St. Paul, Minn. The preferred species, described above, are designated Fluorad FC-95 and FC-98, respectively.

Preferred hydroxyl-containing stabilizing ingredients are open chain aliphatic mono-ols, diols or polyols of from about 1 to about 12 carbon atoms, e.g., methanol, ethanol, iso-propanol, ethylene glycol, propylene glycol, 1,4-butane diol, glycerol, glucose, sucrose, and the like; and closed chain aliphatic or aromatic mono- or di-carboxylic mono-ols, diols or polyols of from about 6 to 12 carbon atoms, e.g., cyclohexanol, cyclohexanediol, inositol, phenol, β-naphthol, resorcinol, sorbitol, hydroquinone, pyrogallol, phloroglucinol, naphthoresorcinol, and the like. It is preferred that these stabilizing ingredients have a water solubility of at least greater than about 4% by weight, especially those in the aromatic family. Particularly preferred stabilizing ingredients of this type are isopropanol, ethylene glycol, glycerol, resorcinol, sorbitol, hydroquinone, pyrogallol and phloroglucinol. These can generally be employed at an appropriate concentration in the range of from about 2 to about 50% by weight in the final mixture. The aromatic compounds will be employed at 2 to 7 wt. percent and the aliphatic compounds will be used in concentrations of from about 4 to 50 wt. percent, although higher and lower amounts can be formulated, as mentioned above. An especially preferred stabilizer is resorcinol at 20 to 70 grams/liter.

Illustrative fluorinated hydrocarbon wetting agents have a formula selected from the group consisting of



and



wherein  $n$  is an integer of from 3 through 10, and Z is a hydrophilic group. Typically such surfactants are composed of molecules containing a perfluorinated tail portion and a hydrophilic head portion. The fluorocarbon portion of the molecules advantageously contains either 3 or 7 carbon atoms where the surfactant is a perfluoro-sulfonic acid derivatives. Thus certain such surfactants have the formula



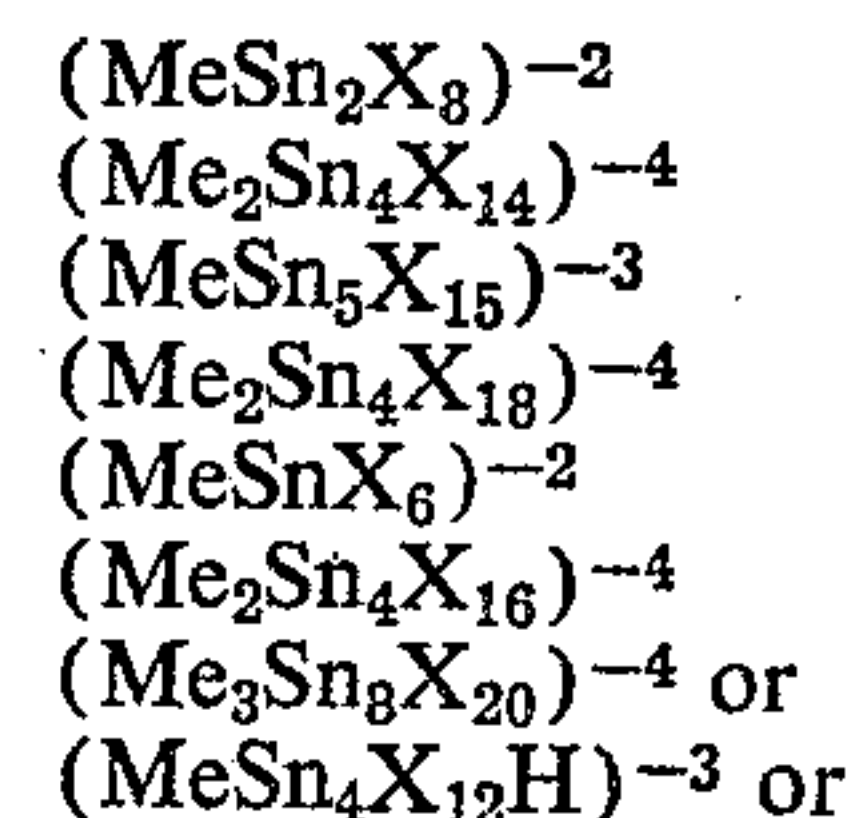
The hydrophilic portion of the fluorocarbon surfactants can be any typical hydrophilic group such as hydroxyl, alkali metal or alkaline earth metal substituted hydroxyl, an alkali metal group, an ammonium group, amine groups, substituted amine groups, quaternary ammonium salts amide and substituted amide groups, and the like.

These can generally be employed at a concentration of from about 0.010 to 5.0 grams per liter in the final mixture, although higher and lower amounts can be formulated. Preferred results are obtained with from 0.025 to 1.0 g./liter and an especially good balance of stability and economy is obtained with 0.05 g./liter of the fluorinated surfactants. An illustrative surfactant for this embodiment of the invention has the formula:



Useful too is hydrogen fluoride itself. This will be employed at 1 to 10 g./liter of solution and preferably at about 3 g./liter. Conveniently, this latter concentration is made by adding enough 60% aqueous HF to provide 50 ml./liter.

While it should not be construed as limiting the invention, it is believed that the complexing reaction which occurs between the metals and the anion results in the formation of more than one and possibly several complexes. Empirically, these can be depicted as including complex anions of the formula



mixtures thereof, wherein Me is Ru, Rh, Pd, Os, Ir, Pt, Au or a mixture thereof, and X is halogen, i.e., fluorine, chlorine, bromine, or iodine; preferably chlorine or bromine. Preferred complexes are those wherein Me is Pd or Pt.

The concentrations of the components of the complexes are expressed in terms of molar ratio. Therefore, the molar ratio of precious metal to Group IV metal to anion of the complexes of the present invention is from about 1:1:3 to 1:6:24.

As is explained above, it is a preferred feature of this invention when preparing particularly preferred sensitizing solutions, most notably those containing complexes of palladium, stannous chloride, to employ an excess of Group IV metal and an excess of the anion. Especially preferred is to use the same anion as component (c).

Sensitizing solutions of the instant invention can be prepared from the solid compositions, which may be stored, and shipped and diluted when the sensitizing solution is to



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be used for electroless plating. When properly prepared, in accordance with the teachings hereof, such diluted solids form true, clear solutions.

The solid compositions of this invention can be prepared in one- or two-steps:

In the one-step preparation, an aqueous mixture, which contains components (a) (b) and (c), as defined above, in which mixture component (a) is present in a concentration of at least about 1.5 grams/liter, the molar ratios of (a) to (b) to (c) each being, respectively 1: at least 1: at least 3; is heated at a temperature of from about 80° C. to about the boiling point of the mixture until formation of the metal complex is substantially complete, then concentrating, e.g., by evaporation, with or without heat, at atmospheric or reduced pressure or by freeze drying, the mixture until a friable, solid product is obtained.

In the two-step preparation, an aqueous solution containing a salt of component (a) in a concentration of from about 1.5 grams per liter up to about the limit of solubility of the salt in water at the boiling point and component (c); and an aqueous solution of component (b) and (c), the ratios of (a):(b):(c) each being respectively, 1: at least about 1: at least about 3, are first prepared. The two solutions are mixed together and heated at a temperature of from about 80° C. to about the boiling point of the mixture until formation of the complex is substantially complete, and then concentrating the mixture until a friable, solid product is obtained. With palladium, 4.8 to 100 grams/liter (calculated as metal) can be conveniently used. Depending on the temperature, it is preferred to heat the mixture for from about 20 to 90 minutes, although this is not critical.

A completely dry product can be made which will be soluble and stable in plain water (as opposed to acid or water and acid) can be prepared by providing:

- (a) the dried complex of (a), (b) and (c) as above defined, e.g., palladium chloride-tin chloride;
- (b) an excess of co-mixed dried stannous chloride;
- (c) a co-mixed dried form of a stabilizer, such as a fluorinated hydrocarbon wetting agent or resorcinol;
- (d) a co-mixed dried source of excess stabilizing and solubilizing anion, e.g., chloride or bromide ion; and
- (e) a co-mixed dried source of acid, such as citric acid.

#### DESCRIPTION OF THE PREFERRED EMBODIMENTS

The following examples are provided for illustrative purposes and may include particular features of the invention. However, the examples should not be construed as limiting the invention, many variations of which are possible without departing from the spirit or scope thereof.

#### EXAMPLE 1

A solid composition, dilutable to an optically clear, sensitizing solution is prepared.

A first solution is prepared comprising the following ingredients:

Palladium chloride (g.)	62.9
Hydrochloric acid (37%, ml.)	200
Water to make total (ml.)	500

A second solution is prepared comprising the following ingredients:

Stannous chloride dihydrate (g.)	800
Hydrochloric acid (37%, ml.)	500

The first solution is added to the second with agitation and the mixture is heated to 85° C. and then boiled in a well ventilated place for one hour.

The mixture is allowed to cool then transferred to a heavy walled suction filtration flask and evaporated under aspirator vacuum until constant weight is obtained. There is obtained a solid composition according to this invention, which is a dark colored friable powder.

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#### EXAMPLE 2

A small quantity of the powdered solid from Example 1 is added to a 12% solution of hydrochloric acid in a test tube. The powder falls to the bottom of the test tube and begins to dissolved. Solution is evidenced by streaks of brown color diffusing away from the vicinity of the dissolving solid. The solution is stirred gently with a glass stirrer rod until uniform and clear. This solution is active to render a piece of epoxy glass laminate receptive to the deposition of electroless copper.

#### EXAMPLE 3

A solid composition, dilutable to an optically-clear sensitizing solution is prepared in one step. The following-formulation is used:

Palladium chloride (g.)	62.5
Hydrochloric acid (37%, ml.)	700
Stannous chloride dihydrate (g.)	800
Water to make total (ml.)	1295

Stannous chloride is dissolved in the hydrochloric acid, then the water is added. The palladium chloride is added with agitation. The mixture is heated to 85° C. for 20 minutes, then boiled for 1.5 hours and cooled. The mixture is evaporated to a friable dark solid by the procedure of Example 1 using a steam bath to assist in water removal.

#### EXAMPLE 4

A first solution is prepared comprising the following ingredients:

Palladium chloride (g.)	10
Hydrochloric acid (37%, ml.)	200
Water to make total (ml.)	500

The palladium salt dissolves slowly in the acid-water mixture.

A second solution is prepared comprising the following ingredients:

Stannous chloride dihydrate (g.)	800
Hydrochloric acid (37%, ml.)	500

The first solution is added to the second with agitation, then the mixture is boiled for 1.5 hours, during which time it changes color from blue or purple, through green, then straw-yellow and, finally, brown.

The mixture is allowed to cool then evaporated to dryness and there is obtained a solid composition according to this invention.

If desired, after cooling and before concentration, 0.8 g. of a fluorocarbon wetting agent (FC-95, 3M Company, St. Paul, Minn.) is added.

In either case the dark product can be diluted with 12% aqueous hydrochloric acid to obtain a highly active sensitizing solution.

#### EXAMPLE 5

The procedure of Example 1 is repeated, respectively substituting for the palladium chloride, stoichiometrically-equivalent amounts of the following: ruthenium chloride ( $\text{RuCl}_3$ ); rhodium chloride ( $\text{RhCl}_3$ ); osmium chloride ( $\text{OsCl}_3$ ); iridium chloride ( $\text{IrCl}_3$ ); and platinum chloride ( $\text{PtCl}_4$ ). Solid compositions according to this invention are obtained containing, respectively, ruthenium, rhodium, osmium, iridium and platinum.

#### EXAMPLE 6

A sensitizing solution according to this invention is prepared by taking an appropriate weight of the composition from Example 1, diluting it with a mixture comprising 490 ml. of 37 percent hydrochloric acid and 490 ml. of water. The resulting solution will contain about 0.6 gram/liter of palladium in the form of the palladium-stannous chloride complex of this invention and will have good catalytic activity.

In a similar manner, catalytically active sensitizing solutions according to this invention are prepared by taking



appropriate portions of the compositions of Example 1 and diluting them, respectively, to 1 liter in 1:1 by volume of a mixture of 37% aqueous hydrochloric acid and water. The solutions contain, respectively, about 0.0003 gram and 1.5 grams of palladium per liter.

#### EXAMPLE 7

The solids of Example 5 are diluted with enough 1:1 mixture by volume of 37% hydrochloric acid and water to provide sensitizing solutions according to this invention containing, respectively, 0.6 and 1.5 grams/liter of ruthenium, rhodium, osmium, iridium and platinum.

It is noted that while the use of stannous chloride is preferred in the practice of the present invention other stannous tin compounds such as, for example, stannous fluoborate and stannous sulfate are also suitable for use in the seeding, i.e., sensitizing compositions described herein and in equivalent concentrations.

invention, after being immersed in the diluted solution

With respect to the sensitizing process aspect of this containing from 0.0005 to 2.5 grams/liter of precious metal for the suitable period of time, the panel surfaces including any side walls of the apertures defined therein are thereafter thoroughly rinsed with water to entirely remove the sensitizing solution therefrom. The panel is then passed through a further bath of lactic acid, suitably diluted, e.g., about 10-20 percent, the passage employing a period of from 10 to 20 seconds, and the panel is again rinsed with water prior to immersion in a suitable electroless plating bath.

Conventional electroless plating baths may be used for the deposition of the adherent metal after sensitizing of the plating surface with the compositions of the present invention. The electroless copper deposition may be followed by electroplating with copper or other metals to build up copper thicknesses of 0.001 to 0.002 inch or greater.

As an example, in the printed circuit industry, electroless copper is ordinarily deposited on apertures formed in plastic insulation sheets which have conductive copper foil laminated on both top and bottom surfaces. Following deposition of electroless copper, the circuits are conventionally electroplated with copper or other metals to build up copper thicknesses of 0.001 to 0.002 inch or greater.

Electroplated copper is required over the electroless copper to form rugged conductive copper on the walls of the aperture approximately 0.001 inch thick or greater. However, in the prior art the adhesion between the electroless copper and the foil originally laminated to the plastic sheet has been very poor due to a poorly adherent flash coating of precious metal from the catalyzing step. The subsequent electrodeposits fail because of the flash coating and could easily be stripped off merely by the application of pressure sensitive adhesive coated cellophane tape such as "Scotch" cellophane tape manufactured by the Minnesota Mining and Manufacturing Company. Therefore, prior to the advent of the present invention, in order to achieve adherent coating, the surface of the copper foil had to be mechanically abraded before electroplating to remove all trace of the electroless copper deposits. This was a costly and time-consuming operation. By using the sensitizing solutions of the present invention, however, it is not necessary to abrade the surface to remove the electroless copper. The electroplated copper may be deposited directly and will adhere so strongly that if the plastic base sheet is broken, the copper foil may be bent back and forth on itself until it breaks but no separation is evident between the original laminated foil and the electroplated copper film.

Although the invention has been described and illustrated by reference to particular embodiments thereof, it will be understood that in its broadest aspects the invention is not limited to such embodiments, and that variations and substitution of such equivalents may be resorted to within the scope of the appended claims.

I claim:

1. A solid composition, dilutable to an optically clear, sensitizing solution for rendering a surface receptive to the deposition of an adherent electroless metal, which comprises a metal complex consisting essentially of:

- (a) an unreduced ion of a precious metal selected from the group consisting of the precious metals of the fifth and sixth periods of Groups VIII and 7-B of the Periodic Table of Elements;
- (b) a Group IV metal of the Periodic Table of Elements which is capable of two valence states; and
- (c) an anion capable of forming a stable moiety with both valence states of the Group IV metal, the molar ratio of components (a) to (b) to (c) being from about 1:3:3 to 1:6:24.

2. A composition as defined in claim 1 which includes, in addition to the amount of component (b) in said complex, a sufficient excess of component (b) to provide from 3 to 100 moles of component (b) per mole of complex in the total composition.

3. A composition as defined in claim 2 wherein said excess of component (b) provides from 5 to 70 moles of component (b) per mole of complex in the total composition.

4. A composition as defined in claim 2 which also includes an excess of component (c) over that present in the complex.

5. A composition as defined in claim 4 in which component (c) is  $\text{Cl}^-$ .

6. A composition as defined in claim 1 which includes an acid in an amount at least sufficient to prevent hydrolysis of the Group IV metal when said composition is diluted.

7. A composition as defined in claim 1 wherein component (a) is palladium.

8. A composition as defined in claim 7 wherein component (b) is tin.

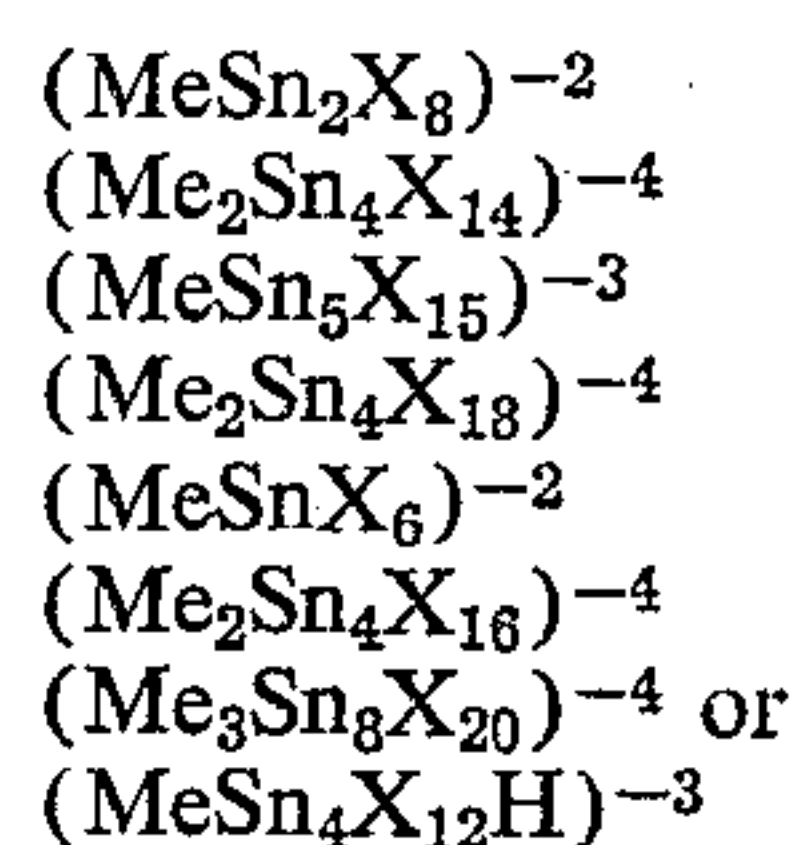
9. A composition as defined in claim 8 wherein component (c) is  $\text{Cl}^-$ ,  $\text{SnCl}_3^-$  or a mixture thereof.

10. A composition as defined in claim 1 wherein component (a) is platinum.

11. A composition as defined in claim 10 wherein component (b) is tin.

12. A composition as defined in claim 11 wherein component (c) is  $\text{Cl}^-$ ,  $\text{SnCl}_3^-$  or a mixture thereof.

13. A solid composition as defined in claim 1 wherein said metal complex includes an anion of the formula:



or a mixture thereof, wherein Me is Ru, Rh, Pd, Os, Ir, Pt, Au or a mixture thereof, and X is halogen.

14. A composition as defined in claim 13 wherein Me is Pd.

15. A composition as defined in claim 13 wherein Me is Pt.

16. A process for the preparation of a solid composition as defined in claim 1 which comprises heating an aqueous mixture containing said components (a), (b) and (c), in which mixture component (a) is present in a concentration of at least about 1.5 grams/liter, at a temperature of from about 80° C. to about the boiling point of said mixture, until formation of said metal complex is substantially complete, then concentrating said mixture until a solid product is obtained.

17. A process for the preparation of a solid composition as defined in claim 1 which comprises

- (1) providing an aqueous solution containing a salt of said component (a) in a concentration of from



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about 1.5 grams per liter up to about the limit of solubility of said salt in water and component (c);  
(2) providing an aqueous solution of said components (b) and (c), the ratios of components (a):(b):(c) being 1: at least 1: at least 3;  
(3) mixing said solutions and heating the mixture at a temperature of from about 80° C. to about the boiling point of said mixture; and  
(4) concentrating the mixture from step (3) until a solid product is obtained.  
18. A solid composition as defined in claim 1 which includes, as a stabilizing ingredient, a compound selected from the group consisting of organic mono-ols, diols and polyols and a fluorinated hydrocarbon wetting agent, the amount of said compound in said composition being at least sufficient to prevent separation from diluted solutions thereof of component (a) as a metallic film or precipitate.

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U.S. Cl. X.R.

106—1, 287 R; 117—47 A, 47 R, 130 E, 160 R; 252—182; 204—30

UNITED STATES PATENT OFFICE  
CERTIFICATE OF CORRECTION

Patent No. 3,672,923 Dated June 27, 1972

Inventor(s) Rudolph J. Zablisky

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 12, line 8, "7" should read -- I --; line 15, "3" (first occurrence) should read -- 1 --; and Column 13, line 15, "cmposition" should read -- composition --.

Signed and sealed this 23rd day of January 1973.

(SEAL)  
Attest;

EDWARD M. FLETCHER, JR.  
Attesting Officer

ROBERT GOTTSCHALK  
Commissioner of Patents