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3,672,938

NOVEL PRECIOUS METAL SENSITIZING SOLUTIONS

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No Drawing. 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 Feb. 20, 1969, Ser. No. 801,167

Int. Cl. C23c 3/02

U.S. Cl. 117-47 A

11 Claims

ABSTRACT OF THE DISCLOSURE

A new and useful precious metal sensitizing solution for rendering surfaces receptive to the deposition of an adherent electroless metal is provided which comprises a metal complex consisting essentially of a precious metal selected from the group consisting of the precious metals of the fifth and sixth periods of Group VIII and I-B of the Periodic Table of Elements, a Group IV metal of the Periodic Table of Elements which is capable of two valence states and an anion capable of forming a stable moiety with both valence states of the Group IV metal, in which the molar ratio of precious metal to Group IV metal to anion is from about 1:1:3 to 1:3:19.

Furthermore, a process for rendering a surface receptive to the deposition of an electroless metal is also provided in which the sensitizing solution hereinabove defined is employed.

CROSS-REFERENCES TO RELATED APPLICATIONS

This application 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 abandoned U.S. application Ser. No. 551,249, filed May 19, 1966, which in turn is a continuation of abandoned U.S. application Ser. No. 285,889, filed June 6, 1963, which in turn is a continuation of abandoned U.S. application Ser. No. 53,352, filed Sept. 1, 1960.

Generally stated, the subject matter of the present invention relates to a new and useful precious metal sensitizing solution. More particularly, the invention relates to a sensitizing solution comprising a precious metal complex, which is useful for rendering surfaces of a substrate catalytic to the reception of an electroless metal.

BACKGROUND OF THE INVENTION

The electroless deposition of a metal to either a metallic or non-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

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two-step process entailing immersion in a stannous chloride solution, followed by immersion in an acid palladium chloride solution. The most recent innovation is a unitary treating process which employs a colloidal dispersion of palladium and tin. See U.S. Pat. No. 3,011,920, Shipley. The plural bath process which readily effecting sensitization deposits a flash coating of precious metal from the sensitizing bath. The 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.

A flash coating of precious metal normally leads to a low grade of adhesion, thereby materially effecting the bond and peel strength, of an electroless metal deposit. The economic consequences of the flash coating then, are the loss of precious metal and the added steps necessary to obviate the effects of such coating.

Accordingly, it is a primary object of the present invention to provide a new composition of matter, as well as a new process 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 compositions and methods for sensitizing substrates which substantially obviate the problem of non-adherent precious metal flash coatings.

It is an additional object of the invention to provide sensitizing compositions and processes which materially reduce the time necessary to effect sensitization.

Yet another object of the invention is to provide compositions and methods for sensitizing substrates with a precious metal which involve using 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.

THE INVENTION

To achieve the foregoing objects, and in accordance with its purposes as embodied and broadly described, the present invention relates to a precious metal sensitizing solution for rendering surfaces receptive to the deposition of an adherent electroless metal which comprises a metal complex consisting essentially of a precious metal selected from the group consisting of the precious metals of the fifth and sixth periods of Group VIII and I-B of the Periodic Table of Elements, a Group IV metal of the Periodic Table of Elements, which is capable of two valence states and an anion capable of forming a stable moiety with both valence states of the Group IV metal, in which the molar ratio of precious metal to Group IV metal to anion is from about 1:1:3 to 1:3:19.

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 solution 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.

The invention then, 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.

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 substantially simultaneously that efficient and uniform deposition of an adhering electroless metal thereon may be readily effected; 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 the copper on the copper foil surfaces of 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 stainless steel, 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, cobalt 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, or a highly viscous paste like composition. Alternately, 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 solutions.

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. Once formed such solutions of the complex may be diluted to levels of concentration which cannot be directly formulated into an active sensitizing solution. In other words the invention makes available sensitizing solutions comprising significantly lower concentrations of precious metal, thereby resulting in lower production costs.

The treating or sensitization procedure described herein is an intermediate step between pretreatment or cleaning of the surfaces upon which the metal is to be electrolessly deposited and the actual deposition 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 soiling 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
5 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 7, 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 a hydrochloric acid solution comprising 42 fluid ounces of hydrochloric acid per gallon of 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 comprises an aqueous solution of a metal complex consisting essentially of a precious metal, a Group IV metal and an anion. Among the precious metals that may be mentioned 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 metal and Group IV metal are palladium and stannous tin. The concentration of the precious metal ion in the sensitizing solution bath should be at least 0.001 gram per liter of solution.

In preparing an acidic sensitizing solution, the salts of the precious metals and of the Group IV metal salt are dissolved in an aqueous solution of suitable acid. Among the acids that may be mentioned are hydrochloric acid, hydrofluoric acid, fluoboric acid, hydroiodic acid, sulfuric acid and acetic acid. Preferably, the anion of the inorganic acid corresponds to the anion of the salt of the precious metals, 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.

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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 concentration of the acid in the sensitizing solution depends upon the strength of the acid employed. The concentration of the acid should be at least 0.001 normal. At the upper end, the concentration 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, be high enough to solubilize the salts of the precious metals and the Group IV metal and also 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 solution.

Lastly, the sensitizing solutions of the present invention may contain additional agents to stabilize the solution 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 wetting agents, such as the fluorinated hydrocarbons. The result of the addition of such agents to the sensitizing solution prevents oxidation of the Group IV metals and the subsequent reduction of the precious metals.

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. The concentrations of the components of the complex then, 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 1:3:19.

It is with the preparation of particular preferred sensitizing solutions, most notably the palladium, stannous chloride solutions, that additional Group IV metal and anion is employed to stabilize the solution. In essence, the preparation of such solutions entails a two-step process in which the complex is first formed and the additional stabilizing portion of stannous chloride is then added. This process is particularly illustrated in Examples I to III inclusive, which demonstrates that the termination of the complexing reaction can be determined by the color of the solution, and at that point the additional stannous and chloride ions are then added.

It has been observed that while stable solutions of palladium, stannous chloride will result from attempts to avoid the two-step process by admixing the stabilizing stannous and chloride ions at the beginning of the complex synthesis, such solutions do not possess the same high degree of activity as those prepared by the two-step process.

The preparation of gold, stannous chloride complex solutions on the other hand, does not require the addition of stannous and chloride ions to stabilize the solutions, and attempts to add additional stannous metal and

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chloride ion to the gold stannous chloride solution have resulted in the formation of colloidal metallic gold.

After being immersed in the sensitizing solution 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 hydrochloric acid, suitably diluted, e.g., about 10 percent of 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 surfaces 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 electroplated copper film and the foil originally laminated to the plastic sheet has been very poor. For example, the electroplated copper 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.

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 I

Preparation of a preferred, palladium, stannous chloride solution

A solution comprising the following ingredients is prepared:

Stannous chloride—8.4 grams
Palladium chloride*—4 grams
Hydrochloric acid (37%)—70 cc.
Water to 1000 cc.

The solution is allowed to sit for approximately one hour at room temperature, during which time the solution will go through several color changes starting with blue-black, then dark green and deep brown and finally

*The palladium chloride is obtained from a solution comprising palladium chloride and hydrochloric acid at a concentration of 50 grams and 50 cc. per liter respectively.

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a dark brown. At this stage it is believed that the solution contains considerable quantities of a catalytically active palladium, stannous chloride complex and requires the addition of 50 grams of stannous chloride. The solution is then diluted with a stannous chloride, hydrochloric acid solution to give a composition having the following concentrations of components:

Palladium chloride.—1 gram/liter
Stannous chloride—60 grams/liter
Hydrochloric acid (37%)—100 cc./liter

The molar ratio for palladium, stannous ion and anion in the above solution is 1:56:330, calculated as follows:

	PdCl ₂	Pd(a)	SnCl ₂	Sn(b)	HCl ¹	Cl(c) ²
Grams/liter.....	1	0.6	60	37.4	43.5	65.5
Moles/liter.....		0.0056		0.316		1.846

¹ 100 cc. X 1.18 sp. gr. X 37% conc.

² Based on PdCl₂ + SnCl₂ + HCl.

$$\text{Molar ratio} = \frac{a}{a} : \frac{b}{a} : \frac{c}{a} = \frac{0.0056}{0.0056} : \frac{0.316}{0.0056} : \frac{1.846}{0.0056} = 1:56:330$$

The solution is catalytically active and will remain stable so long as the stannous tin and hydrochloric acid are maintained.

If the additional 50 grams of stannous chloride is not added to the original solution when it achieves a dark brown color, the solution will be unstable and a black precipitate will form after standing for several days. The black precipitate is believed to contain a palladium, stannous complex and palladium metal. The precipitated complex can be redissolved in concentrated hydrochloric acid and will be catalytically active. To achieve stability excess stannous tin should be added to the solution.

The precipitated palladium metal will not redissolve in the concentrated hydrochloric acid unless an oxidizing agent such as hydrogen peroxide is added.

EXAMPLE II

Preparation of a dilute sensitizing solution

Prepare a solution comprising the following ingredients:

Palladium chloride—20 grams
Hydrochloric acid (37%)—400 cc.
Water to 100 cc.

In a separate container dissolve 800 grams of stannous chloride in 500 cc. of 37 percent hydrochloric acid. To this solution add 500 cc. of the first solution with agitation and heat the mixture in a well ventilated place to 85° C. or higher with agitation to maintain uniform heating.

The mixture is then allowed to cool and 120 cc. of the mixture is added with stirring, to a solution comprising 430 cc. of 37 percent hydrochloric acid and 450 cc. of water. The resulting solution will contain a high concentration of the preferred palladium, stannous chloride complex and will have good catalytic activity. The dilute solution consists of the following concentrations of components:

Palladium chloride—1 gram/liter
Stannous chloride—80 grams/liter
Hydrochloric acid (37%)—500 cc./liter

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The molar ratio for palladium, stannous ion and anion in the above solution is 1:76:1220, calculated as follows:

	PdCl ₂	Pd(a)	SnCl ₂	Sn(b)	HCl ¹	Cl(c) ²
Grams/liter.....	1	0.6	80	50.2	218	242.5
Moles/liter.....		0.0056		0.425		6.86

¹ 500 cc. X 1.18 sp. gr. X 37% conc.

² Based on PdCl₂ + SnCl₂ + HCl.

$$\text{Molar ratio} = \frac{a}{a} : \frac{b}{a} : \frac{c}{a} = \frac{0.0056}{0.0056} : \frac{0.425}{0.0056} : \frac{6.86}{0.0056} = 1:76:1,220$$

An additional dilute solution is prepared in substantially the same manner as hereinabove described, having both a high concentration of the preferred complex, as well as good catalytic activity. The dilute solution consists of the following concentrations of components:

Palladium chloride—0.05 gram/liter
Stannous chloride—5 grams/liter
Hydrochloric acid (37%)—350 cc./liter

The molar ratio for palladium, stannous ion and anion in the above solution is 1:86:14,000, calculated as follows:

	PdCl ₂	Pd(a)	SnCl ₂	Sn(b)	HCl ¹	Cl(c) ²
Grams/liter.....	0.05	0.03	5	3.13	153	150.9
Moles/liter.....		.0003		0.026		4.254

¹ 350 cc. X 1.18 sp. gr. X 37% conc.

² Based on PdCl₂ + SnCl₂ + HCl.

$$\text{Molar ratio} = \frac{a}{a} : \frac{b}{a} : \frac{c}{a} = \frac{0.0003}{0.0003} : \frac{0.026}{0.0003} : \frac{4.254}{0.0003} = 1:86:14,000$$

Attempts to duplicate a catalytically active solution comprising the above concentrations of components directly will not be successful.

The solution is prepared by dissolving 1 gram of palladium chloride in water containing 200 cc. of 37 percent hydrochloric acid and then dissolving 80 grams of stannous chloride in the solution. The resulting solution is not catalytically active even though a palladium, stannous chloride complex is formed as will be evidenced by the fact that the original palladium chloride, hydrochloric acid solution loses its original properties. In essence, the palladium chloride, hydrochloric acid solution will have a light yellow color and will galvanically deposit palladium metal on a strip of copper metal. The addition of stannous chloride will change the color of the solution to deep green and the solution will no longer galvanically deposit palladium metal on a strip of copper.

EXAMPLE III

Preparation of a gold stannous chloride solution

A solution is prepared comprising the following ingredients:

Gold chloride solution 2%—5 cc.
Stannous chloride—17 grams
Hydrochloric acid (37%)—50 cc.
Water—to 1000 cc.

Dissolve the stannous chloride in water and add the hydrochloric acid. To this solution add the gold chloride solution with agitation. A small amount of precipitate forms, which is removed, and the remaining solution comprises the gold, stannous chloride complex. The solution is catalytically active.

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Preparation of a palladium, stannous chloride sensitizing solution

A sensitizing solution comprising the following ingredients is prepared:

Palladium chloride (PdCl₂)—0.25–1 gram
Hydrochloric acid (HCl) (37% solution)—40–60 cc.
Stannous chloride (SnCl₂·2H₂O)—12–22 grams
Water to 1000 cc.

The molar ratios for palladium (Pd), stannous ion (Sn) and anion (Cl) in the above solutions are 1:9.5:104:650, calculated as follows:

	PdCl ₂	Pd(a)	SnCl ₂ ·2H ₂ O	Sn(b)	HCl ¹	Cl(c) ²
G./l.-----	0.25-1	0.15-0.6	12-22	6.3-11.6	17.5-26.2	20.9-32.8
Mo./l.-----	.0014-.0056	.0014-.0056		.054-.098		.59-.92

¹ 40-60 cc.×1.18 sp. gr.×37% conc.

² Based on PdCl₂ + SnCl₂ + HCl.

$$\text{Molar ratio} = \frac{a \cdot b \cdot c}{a' \cdot a' \cdot a'}$$

$$\text{minimum molar ratio} = \frac{0.0056 \cdot 0.054 \cdot 0.59}{0.0056 \cdot 0.0056 \cdot 0.0056} = 1:9.5:104;$$

and

$$\text{maximum molar ratio} = \frac{0.0014 \cdot 0.098 \cdot 0.921}{0.0014 \cdot 0.0014 \cdot 0.0014} = 1:70:650$$

This composition is formulated by the dissolving palladium chloride in water containing 40 to 60 cc. of 37 percent of 1 N hydrochloric acid. Dissolution is slow and continues normally for several hours at room temperature. When the palladium is completely dissolved the stannous chloride is dissolved in the resulting solution. It is noted in this regard that when the stannous chloride is first dissolved in the aforesaid solution a green color may be noticed initially. After about one hour, however, the solution will change to a dark brown color, which coloration indicates that the solution, which is made up of 1 liter with water, is ready for use. The panel being prepared for plating is then immersed in the sensitizing solution for a period of from 5 to 20 minutes at room temperature.

Concentrates of the sensitizing solution can be separately prepared for use when desired. In this embodiment, a concentrated solution of palladium chloride and hydrochloric acid is made and a separate concentrated solution of stannous chloride and hydrochloric acid also prepared. When the two solutions are reacted and diluted to form the sensitizing solution of the present invention, the concentration of hydrochloric acid present therein is adjusted to within the concentration recited above, e.g., 40 to 60 cc. of 37 percent hydrochloric acid per liter of solution.

If a single concentrate is prepared containing both palladium chloride and stannous chloride, in addition to hydrochloric acid, the concentration of palladium chloride should be kept below about 4 grams per liter, otherwise the palladium ions will reduce to metallic palladium. This concentrated solution is normally diluted to within the hydrochloric acid concentration range recited above, prior to use.

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 compositions described herein and in equivalent concentrations.

EXAMPLE V

Low acid content sensitizing solution

The following is an example of a suitable sensitization solution having low acid content:

Palladium chloride—1 gram
Stannous chloride—20 grams
Hydrochloric acid (37%)—1 cc.
Water to 1000 cc.

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The molar ratio for palladium, stannous ion, and anion in the above solution is 1:19:42, calculated as follows:

	PdCl ₂	Pd(a)	SnCl ₂	Sn(b)	HCl ¹	Cl(c) ²
Grams/liter-----	1.0	0.6	20	12.6	0.425	8.34
Moles/liter-----		0.0056		0.106		0.235

¹ 1 cc.×1.18 sp. gr.×37% conc.

² Based on PdCl₂ + SnCl₂ + HCl.

$$\text{Molar ratio} = \frac{a \cdot b \cdot c}{a' \cdot a' \cdot a'} = \frac{0.0056 \cdot 0.106 \cdot 0.235}{0.0056 \cdot 0.0056 \cdot 0.0056} = 1:19:42$$

EXAMPLE VI

High acid content sensitizing solution

The following is an example of a suitable sensitization solution having high acid content:

Palladium chloride—4 grams
Stannous chloride—25 grams
Hydrochloric acid (37%)—1 liter

The molar ratio for palladium, stannous ion and anion in the above solution is 1:6:540, calculated as follows:

	PdCl ₂	Pd(a)	SnCl ₂	Sn(b)	HCl ¹	Cl(c) ²
Grams/liter-----	4	2.4	25	15.7	436	435
Moles/liter-----		0.023		0.132		11.9

¹ 1,000 cc.×1.18 sp. gr.×37% conc.

² Based on PdCl₂+SnCl₂+HCl.

$$\text{Molar ratio} = \frac{a \cdot b \cdot c}{a' \cdot a' \cdot a'} = \frac{0.023 \cdot 0.132 \cdot 11.9}{0.023 \cdot 0.023 \cdot 0.023} = 1:6:540$$

EXAMPLE VII

Use of stannous fluoborate

The following is an example of stannous fluoborate compositions which may be used as the sensitizing solution:

Palladium chloride—1 gram
Fluoboric acid (HBF₄—49% solution)—50 cc.
Stannous fluoborate [Sn(BF₄)₂—47% solution]—10 cc.
Water to 1000 cc.

The molar ratio for palladium, stannous ion and anion (BF₄⁻ and Cl⁻) in the above solution is 1:23:62, calculated as follows:

	PdCl ₂	Pd(a)	SnBF ₄ ¹	Sn(b)	HBF ₄ ²	Anion(c) ³
Grams/liter---	1	0.4	38	15.4	6.7	29.6
Moles/liter-----		0.0056		0.129		0.347

¹ 50 cc.×1.6 sp. gr.×47% conc.

² 10 cc.×1.37 sp. gr.×49% conc.

³ Based on PdCl₂+Sn(BF₄)₂+HBF₄.

$$\text{Molar ratio} = \frac{a \cdot b \cdot c}{a' \cdot a' \cdot a'} = \frac{0.0056 \cdot 0.129 \cdot 0.347}{0.0056 \cdot 0.0056 \cdot 0.0056} = 1:23:62$$

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Use of stannous sulfate

The following is an example of stannous sulfate compositions which may be used as the sensitizing solution:

Palladium chloride—4 grams
Sulfuric acid (98%)—140 cc.
Stannous sulfate—20 grams
Water to 1000 cc.

The molar ratio for the palladium, stannous ion and anion (SO₄⁼ and Cl⁻) in the above solution is 1:4:118, calculated as follows:

	PdCl ₂	Pd(a)	SnSO ₄	Sn(b)	H ₂ SO ₄ ¹	Anion (c) ²
Grams/liter...	4	2.4	20	11	250	257.1
Moles/liter.....		0.023		0.093		2.72

¹ 140 cc. X 1.86 sp. gr. X 98% conc.

² Based on PdCl₂+SnSO₄+H₂SO₄.

$$\text{Molar ratio} = \frac{a \cdot b \cdot c}{a' \cdot a'' \cdot a'''} = \frac{0.023 \cdot 0.023 \cdot 2.72}{0.023 \cdot 0.023 \cdot 0.023} = 1:4:118$$

The stannous fluoborate and stannous sulfate sensitizing solutions are made up in a manner similar to that described hereinabove in connection with the stannous chloride solutions.

The following examples further illustrate typical sensitizing solutions of the present invention.

EXAMPLE IX

Platinum chloride—1 gram
Stannous chloride—20 grams
Hydrochloric acid (37%)—40 cc.
Water to 1000 cc.

The molar ratio for platinum, stannous ion and anion in the above solution is 1:28:184, calculated as follows:

	PtCl ₂	Pt(a)	SnCl ₂	Sn(b)	HCl ¹	Cl(c) ²
Grams/liter.....	1.0	0.73	20	12.55	17.5	24.8
Moles/liter.....		.0038		0.106		0.70

¹ 40 cc. X 1.18 sp. gr. X 37% conc.

² Based on PtCl₂+SnCl₂+HCl.

$$\text{Molar ratio} = \frac{a \cdot b \cdot c}{a' \cdot a'' \cdot a'''} = \frac{0.0038 \cdot 0.106 \cdot 0.70}{0.0038 \cdot 0.0038 \cdot 0.0038} = 1:28:184$$

EXAMPLE X

Auric chloride—1 gram
Stannous chloride—20 grams

EXAMPLE XI

Rhodium chloride—4 grams
Stannous chloride—20 grams
Hydrochloric acid (37%)—40 cc.
Water to 1000 cc.

The molar ratio for rhodium, stannous ion and anion in the above solution is 1:5.6:40, calculated as follows:

	RhCl ₃	Rh(a)	SnCl ₂	Sn(b)	HCl ¹	Cl ₂ (c) ²
Grams/liter.....	4.0	1.98	20	12.55	17.5	26.5
Moles/liter.....		0.019		0.106		0.75

¹ 40 cc. X 1.18 sp. gr. X 37% conc.

² based on RhCl₃+SnCl₂+HCl.

$$\text{Molar ratio} = \frac{a \cdot b \cdot c}{a' \cdot a'' \cdot a'''} = \frac{0.019 \cdot 0.106 \cdot 0.75}{0.019 \cdot 0.019 \cdot 0.019} = 1:5.6:40$$

12 EXAMPLE XII

Palladium chloride—1 gram
Acetic acid (99.5%)—880 cc.
Stannous chloride—20 grams
Water to 1000 cc.

The molar ratio for palladium, stannous ion and anion (CH₃CO₂⁻+Cl⁻) in the above solution is 1:18.8:2800, calculated as follows:

	PdCl ₂	Pd(a)	SnCl ₂	Sn(b)	HAC ¹	Anion (c) ²
Grams/liter.....	1	0.6	20	12.55	920	912.9
Moles/liter.....		0.0056		0.106		15.5

¹ Acetic acid—880 cc. X 1.05 sp. gr. X 99.5%.

² Based on PdCl₂+SnCl₂+acetic acid.

$$\text{Molar ratio} = \frac{a \cdot b \cdot c}{a' \cdot a'' \cdot a'''} = \frac{0.0056 \cdot 0.106 \cdot 15.5}{0.0056 \cdot 0.0056 \cdot 0.0056} = 1:18.8:2,800$$

The solutions of Examples IX and XII are made up in a manner similar to that described in Example I.

As will be noted from Examples I-II, IV-IX and XI-XII above, the minimum molar ratio of precious metal ion to stannous ion to anion in the solution will be 1:4:40; and the minimum molar ratio of palladium to tin to chloride in solutions of the preferred PdCl₂·SnCl₂ reaction product, Examples IV-VI, will be approximately 1:6:42.

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.

What is claimed is:

1. A process for sensitizing a substrate to be plated with an adherent electroless metal which comprises cleaning said substrate and contacting said cleaned substrate with a sensitizer solution consisting of an effective amount of a metal complex dissolved in said solution, said complex consisting essentially of an unreduced ion of a precious metal selected from the group consisting of the precious metals of the fifth and sixth periods of Group VIII and I-B of the Periodic Table of Elements, an ion of a Group IV metal of the Periodic Table of Elements which is capable of two valence states, and an anion capable of forming a stable moiety with both valence states of the Group IV metal, the molar ratio of precious metal to Group IV metal to anion being from about 1:1:3 to 1:3:19.

2. A process according to claim 1 in which the metal complex is palladium, stannous chloride.

3. A process for sensitizing a substrate according to claim 1 in which the sensitizer solution contains a wetting agent.

4. A process for electrolessly plating an adherent metal deposit on a substrate which comprises sensitizing said substrate by contacting same with a sensitizer solution consisting of an effective amount of a metal complex dissolved in said solution, said complex consisting essentially of an unreduced ion of a precious metal selected from the group consisting of the precious metals of the fifth and sixth periods of Group VIII and I-B of the Periodic Table of Elements, an ion of a Group IV metal of the Periodic Table of Elements which is capable of two valence states, and an anion capable of forming a stable moiety with both valence states of the Group IV metal, the molar ratio of precious metal to Group IV metal to anion being from about 1:1:3 to 1:3:19, substantially entirely removing the sensitizer solution by rinsing said substrate with water, thereafter contacting said substrate with a dilute hydrochloric acid solution, and again rinsing with water, and then contacting said substrate with an electroless metal plating bath and electrolessly depositing metal on said sensitized substrate.

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5. A process according to claim 4 in which the electroless metal is copper.

6. A process for electrolessly plating an adherent metal deposit on a substrate according to claim 4 in which the sensitizer solution contains a wetting agent.

7. A sensitizer solution for sensitizing a surface to the deposition of an adherent electroless metal, the solution consisting essentially of an effective amount of unreduced ions of palladium, chloride anions and stannous tin ions in an amount sufficient to react with said unreduced ions of palladium and form with said palladium ions, a $\text{PdCl}_2 \cdot \text{SnCl}_2$ reaction product dissolved in said sensitizer solution, the solution being acidic and free of reduced palladium and containing stannous tin ions and chloride anions unreacted with said reaction product, the minimum molar ratio of palladium to tin to chloride in said solution being about 1:6:42.

8. A sensitizer solution according to claim 7 which includes a wetting agent.

9. A process for sensitizing a substrate to be plated with an adherent electroless metal which comprises contacting said substrate with a sensitizer solution as defined in claim 7.

10. A process for electrolessly plating an adherent metal deposit on a substrate which comprises sensitizing said substrate by contacting same with a sensitizer solu-

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tion as defined in claim 7, and then contacting said substrate with an electroless metal plating bath and electrolessly depositing metal on said sensitized substrate.

11. A process according to claim 10 in which the electroless metal being deposited is copper.

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U.S. Cl. X.R.

117-47 R, 130 E, 160 R; 106-1