

[54] **CATALYST SOLUTION FOR ELECTROLESS DEPOSITION OF METAL ON SUBSTRATE**

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[22] Filed: **Nov. 14, 1973**

[21] Appl. No.: **415,526**

Related U.S. Application Data

[63] Continuation-in-part of Ser. Nos. 224,742, Feb. 9, 1972, abandoned, and Ser. No. 374,093, June 27, 1973.

[52] U.S. Cl. **106/1, 117/47 A, 204/30**

[51] Int. Cl. **C23c 3/00**

[58] Field of Search **106/1; 117/47 A; 204/30**

References Cited

UNITED STATES PATENTS

3,627,558	12/1971	Roger et al.	117/47 R
3,650,913	3/1972	D'Ottavio	117/47 A
3,672,923	6/1972	Zeblisky.....	106/286

3,698,919	10/1972	Kuzmik.....	106/1
3,767,583	10/1973	Fadgen et al.	106/1

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[57] ABSTRACT

The invention described herein is a catalyst for activating a substrate for the initiation of electroless metal plating and to a process for making the same. The catalyst comprises the product resulting from the admixture of an acid soluble salt of a catalytic metal; the addition product believed to be formed from a solution soluble stannous salt, an acid and urea; and preferably, an extraneous source of halide ions. The catalyst of the invention differs from prior art catalysts in that it has greater stability, does not fume, is lower in cost to make and use and, in the preferred embodiment employing the extraneous source of halide ions, may be operated at lower acidity (high pH) than the prior art catalysts.

68 Claims, 4 Drawing Figures

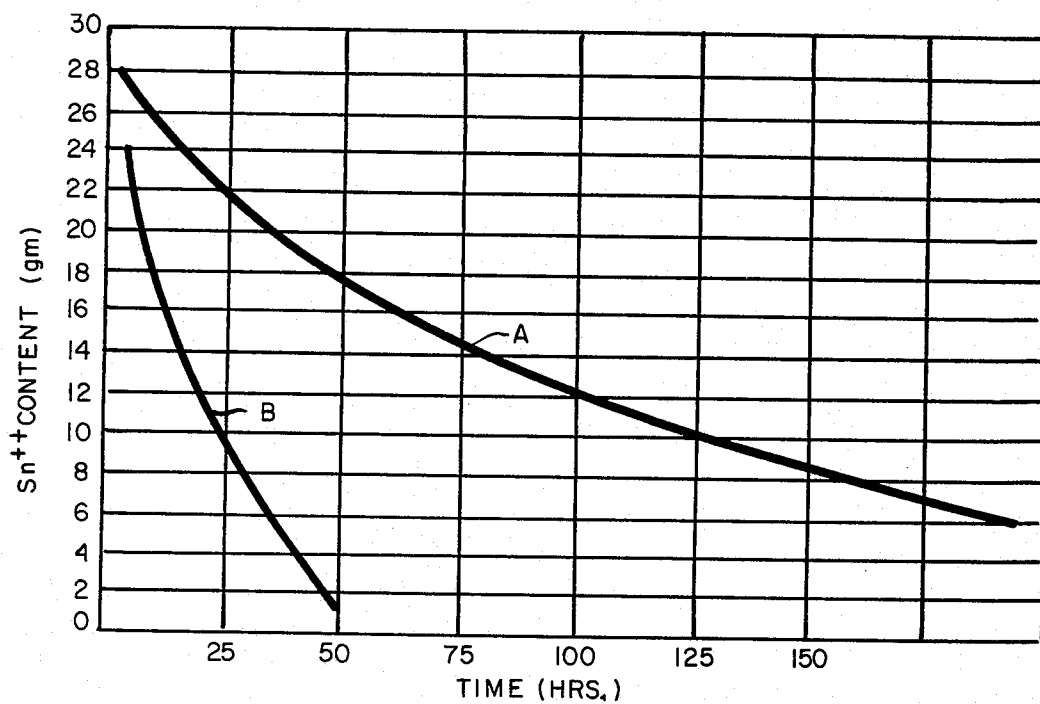


FIG. 1

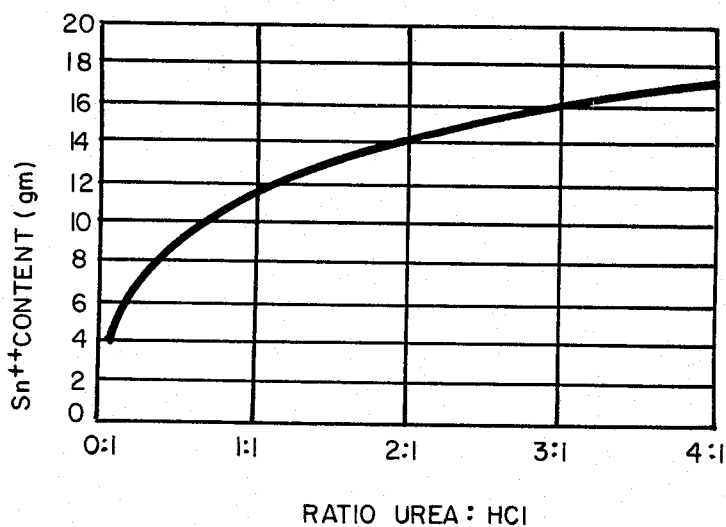


FIG. 2

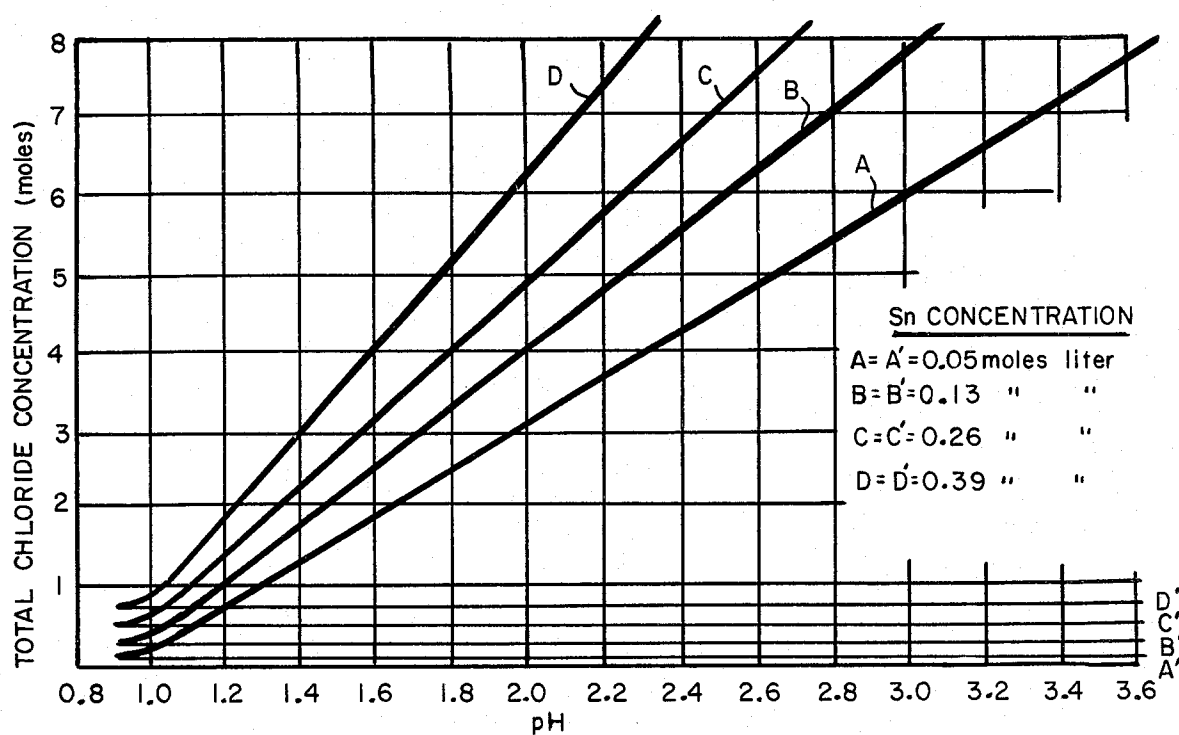


FIG.3

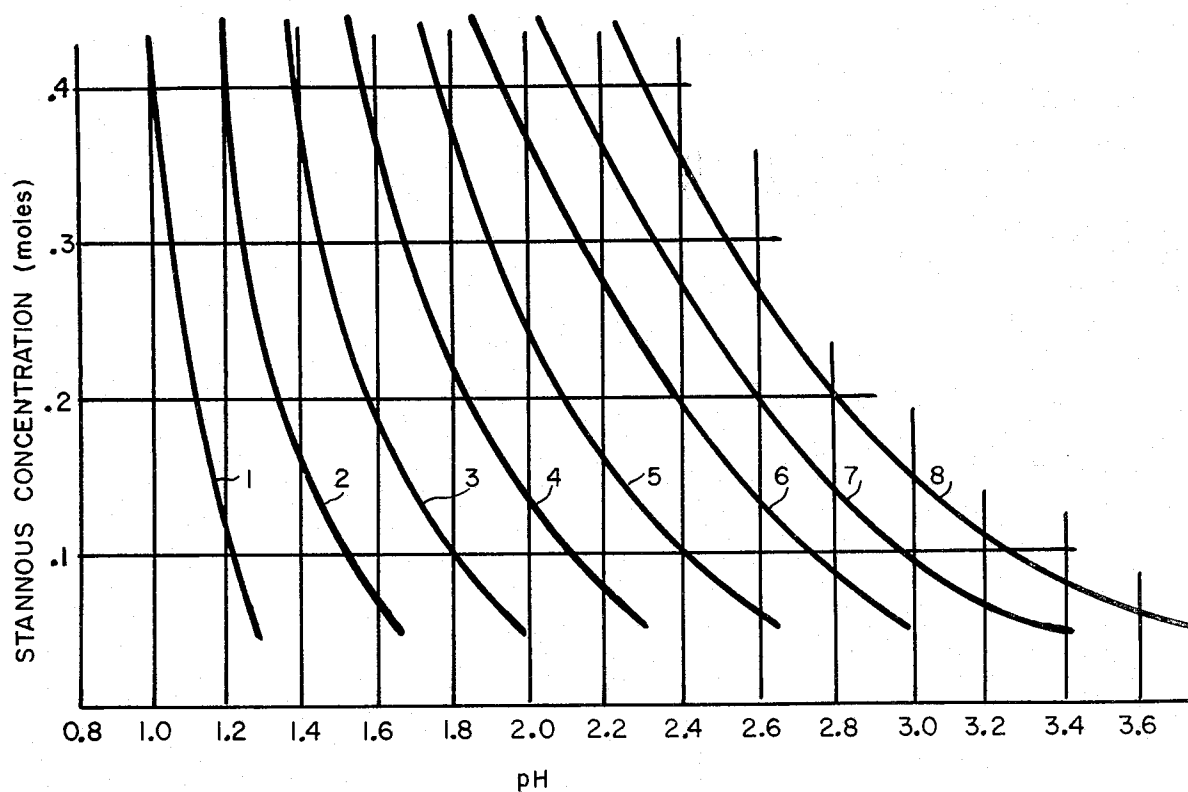


FIG.4

CATALYST SOLUTION FOR ELECTROLESS DEPOSITION OF METAL ON SUBSTRATE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of our co-pending U.S. patent applications Ser. Nos. 224,742 filed on Feb. 9, 1972, now abandoned, and 374,093, filed on June 27, 1973.

BACKGROUND OF THE INVENTION

1. Introduction

This invention is directed to a formulation for catalyzing a substrate prior to electroless metal deposition.

2. Description of the Prior Art

For electroless plating of substrates, especially for the plating of non-conductive substrates, it has been known for some time that chemically plated metal deposits of suitable thickness and adequate bond strength are commercially practical only if the substrate surface is properly catalyzed prior to metal deposition.

A common method for catalyzing a substrate prior to plating involves contact of the substrate with two solutions known in the art as a two-step catalyst. A process for metallizing utilizing this catalyst comprises contact of a substrate with a first acidic aqueous solution of a reducing agent such as stannous chloride followed after water rinse by contact with a second solution of a catalytic metal salt such as palladium chloride in dilute hydrochloric acid. The adsorbed reducing agent reduces the catalytic metal ions in situ on the substrate surface to the catalytic metal thereby providing catalytic sites on the surface which sites are receptive to electroless metal deposition thereon. This procedure is employed successfully in many plating-on-plastic applications. However, it is subject to various disadvantages including poor adhesion between a metallic substrate surface such as copper and a subsequently applied metal deposit. This is especially true where copper is to be deposited over copper such as in the manufacture of printed circuit boards where copper is deposited over both a plastic substrate and a copper cladding over said plastic substrate. Also, articles in the process of being plated using the aforesaid two-step catalyst must be re-racked subsequent to catalysis before proceeding to additional steps in the plating sequence to avoid contamination of the catalyst through drag-in from preceding steps and rapid deterioration of the plating bath. Metal plate for decorative purposes obtained using the two-step catalyst exhibits star dusting—i.e., minor imperfections on the surface of the metal plate.

An alternative method for catalyzing a substrate prior to electroless deposition is also known and is disclosed and claimed in U.S. Pat. No. 3,011,920 incorporated herein by reference. In this method, a substrate is contacted with a colloidal catalytic solution formed by the admixture in acid solution of a catalytic metal salt, a stannous salt in molar excess of the catalytic metal salt and a hydrohalide acid. The catalytic metal may be selected from the group of silver, gold and the platinum family of metals. Palladium is the preferred catalytic metal. The excess stannous salt is responsible for stability of the colloid and prevents it from precipitating out of its suspension. The catalyst operates at a pH below about 1 and preferably well below 0. The limitation on the pH is due to the fact that the stannous salt hydrolyzes and precipitates at a pH of about 0.9.

Though this colloidal catalyst has been widely accepted and preferred for most applications, it is not without some difficulties. One such difficulty is the gradual loss of stannous ion in highly acidic solution by a process believed to involve aerial oxidation with the formation of stannic ion leading to catalyst instability and subsequent loss. Another such difficulty is the attack of the highly acidic solution of various substrate materials with which the catalyst comes into contact, especially plastic materials including the plastic racks used to carry the substrate through the plating sequence. Another difficulty is the volatilization of the hydrohalide acid which is undesirable from a health standpoint, corrosion of surroundings, and a quality control standpoint. Both of these latter problems would be overcome if the catalyst formulation could be prepared at a pH higher than the pH of the catalyst formulations of the prior art.

In U.S. Pat. No. 3,672,938, there is disclosed a process for catalyzing a substrate prior to electroless metal deposition with a catalyst also formulated by the admixture in acid solution of a catalytic metal salt, a stannous salt in molar excess of the catalytic metal salt and a hydrohalide acid. This catalyst is said to differ from the catalyst of U.S. Pat. No. 3,011,920 in physical form, it being asserted that the catalyst of said patent is a "true solution catalyst" rather than a colloidal catalyst as in the aforesaid U.S. Pat. No. 3,011,920. Regardless of its physical form, it is also highly acidic and suffers the same disadvantages as the catalyst of said U.S. Pat. No. 3,011,920.

No attempts are known to have been made in the prior art to prevent the loss of stannous ion by aerial oxidation. Attempts have been made to formulate a low acid, high pH catalyst. Such attempts have been unsuccessful because the low acid catalyst has been formulated by the expedient of reducing the hydrohalide acid content. Such a reduction results in the formation of a precipitate at a pH of about 0.9 for a chloride system. This formation of precipitate is believed to be due to hydrolysis of the stannous ions with the formation of insoluble hydrolysis products. This results in loss of the catalyst. An example of this is shown in the aforesaid U.S. Pat. No. 3,672,938, Example V, where there is disclosed a catalyst having a total acid content of one milliliter of concentrated hydrochloric acid per liter of solution. This formulation is of no commercial value as it is of insufficient acidity to solubilize the stannous salt and consequently a stable colloidal catalyst or stable catalyst in any other form, should it exist, cannot be prepared.

DEFINITIONS

The following definitions are provided to assist in the understanding of the ensuing text:

"Catalyst formulation" is the product resulting from the admixture of an acid soluble salt of a catalytic metal, a stannous salt in molar excess typically in substantial excess, of the catalytic metal salt, an acid, urea and preferably an extraneous source of halide ions.

"Catalyst component" refers to any one or more of the salts of the catalytic metal, stannous salt or acid used in making the catalyst formulation.

"Addition Product" refers to the product that is believed to be formed by the admixture of the stannous salt, the acid and urea. This is called an addition product because empirical evidence in connection with the

properties of the catalyst suggests that such an addition product is formed. However, it is possible that only two of the three aforesaid ingredients form such an addition product or alternatively, no addition product is formed at all, each of the three ingredients existing independently in solution. Accordingly, as used herein, the term addition product encompasses the three ingredients used for the purposes set forth herein without limitation as to the manner in which they interact, if at all.

"Actual halide ion concentration" is the concentration of the halide ions in the catalyst formulation, if any, of the catalyst components used in the form of a halide. This will be zero if none of the aforesaid components are used in the form of a halide.

"Maximum component halide ion concentration" is the concentration of halide ions that would be in the catalyst formulation if each of the catalyst components were used in the form of the halide.

"Total halide ion concentration" is the required amount of halide ions in the catalyst formulation in accordance with this invention.

"Extraneous halide ions" and like terms mean a source of halide ions in addition to those supplied by the catalyst components. The concentration of the extraneous halide ions is equal to the difference between the total halide ion concentration and the actual halide ion concentration.

"Excess halide ions" are halide ions in the catalyst in excess of the maximum component halide ion concentration and the concentration of the excess halide ions is equal to the difference between the total halide ion concentration and the maximum component halide ion concentration. The concentration of the excess halide ions equals the concentration of the extraneous halide ions when all of the catalyst components used to make the catalyst are in the form of the halide.

"Precipitation point" is the pH at which a precipitate forms in the catalyst formulation rendering the catalyst unsuitable for use. This precipitate is believed to be hydrolysis products, principally of the stannous salt.

SUMMARY OF THE INVENTION

The catalysts described herein are improvements over catalysts such as those described and claimed in the aforesaid U.S. Pat. Nos. 3,011,920 and 3,672,938 in that they have greater solution stability, minimal loss of stannous ion even at low pH, better adsorption properties, and, if desired, a decreased hydrogen ion concentration with a correspondingly high pH.

The invention is predicated in part upon the discovery that urea addition to the catalyst formulation minimizes stannous ion oxidation loss and consequently, catalyst instability and halide ions play a significant role in the functioning of the catalyst, the catalyst being improved when the concentration of halide ions is increased beyond that concentration found in the prior art catalysts by the addition of an extraneous source of halide ions. The improvements resulting from the addition of urea to the formulation preferably coupled with an excess halide ion concentration comprise improved stability and adsorption properties and solubilization of the stannous salt or retardation of the precipitation point. Accordingly, catalysts of increased stability and pH can be formulated thereby providing catalyst suitable for use with materials readily attacked by strong acids.

A catalyst composition in accordance with this invention comprises the product resulting from the admixture of (1) an acid soluble salt of a catalytic metal, (2) the addition product formed from a solution soluble stannous salt in molar excess of the catalytic metal salt, an acid urea and preferably (3) an extraneous source of halide ions in an amount sufficient to provide an excess of halide ions in the formulation. The catalyst formulations of this invention have a pH of less than about 3.5 dependent upon the stannous content as will be explained in greater detail below.

The product resulting from the admixture of the stannous salt, hydrohalide acid and urea (2 above) as noted above, is believed to be the addition product which undergoes only minimal dissociation in solution. It appears that as a result of this minimal dissociation, the hydrohalide acid is not available for loss by fuming and the stannous ion is unavailable for loss by oxidation. It is an unexpected discovery of this invention that these components can be used in the form of the addition product without adversely affecting the properties of the catalyst, even though the product undergoes only minimal dissociation.

In addition to the above, there are unexpected secondary advantages to the invention. For example, since there is no fuming of the hydrohalide acid, there is essentially no odor associated with the use of the catalyst. Also, use of the catalyst is less costly because of the decreased need for replenishment of either the stannous salt or the hydrohalide acid. This also means decreased volume growth of the catalyst due to replenishment. Furthermore, by maintaining the stannous content and hydrohalide acid content substantially constant in accordance with the invention, the results obtainable upon plating—e.g., bond strength, take-off, coverage and the like are more reliable and predictable.

DESCRIPTION OF THE DRAWINGS

In the drawings, FIG. 1 of the drawings is a graphical comparison of stability of a catalyst solution with and without the use of the addition product of this invention;

FIG. 2 is a graphical representation of urea content in the formation of the addition product as a function of stability;

FIG. 3 graphically represents precipitation point of a series of catalysts as a function of pH; and

FIG. 4 graphically represents the precipitation point of a series of catalysts as a function of stannous ion concentration.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention set forth herein comprises a catalyst which includes (1) an acid soluble salt of a catalytic metal, (2) the addition product of a stannous salt soluble in aqueous solution in molar excess of the catalytic metal, an acid and urea and preferably, (3) an extraneous source of halide ion in an amount sufficient to provide an excess of halide ions in the formulation.

The catalyst may be formulated substantially with materials and in proportions such as those described and claimed in the aforesaid U.S. Pat. Nos. 3,011,920 and 3,672,938. The acid soluble salt of the catalytic metal is a salt of any of those metals known to exhibit catalytic properties in chemical plating. Such metals include the precious metals, gold and silver and mem-

bers of the platinum family. Palladium is generally found to be the most satisfactory of these catalytic metals for the activation of a non-conducting substrate, particularly a plastic substrate, and therefore constitutes the preferred embodiment of this invention. Silver, gold and rhodium constitute lesser preferred embodiments of the invention as some difficulty is encountered in the preparation of the catalyst due to limited solubility of the silver salts and instability of the gold and rhodium salts in solution.

The particular salt of the catalytic metal used is not critical and may comprise the halides such as those described in the aforesaid U.S. Pat. No. 3,011,920 as well as such other salts as the nitrate, sulfate and the like. Fluoride and iodide salts are lesser preferred. Salts other than halides are suitable as halide ions may be introduced into solution by the extraneous source of halide ions. Preferably, the salt is the halide having an anion common to that of the other catalyst components. It should be noted that when the halide salt is used, some halide is introduced into solution, but because of the low concentration of the catalytic metal salt used, this amount is generally negligible.

The amount of the catalytic metal salt is not critical and is primarily governed by cost and functional considerations. Thus, though up to 40 to 50 grams per liter or more of the catalytic metal salt is possible, it is desirable to maintain the quantity of the salt as low as possible from a cost consideration without sacrificing the functional properties of the catalytic formulation. Typically, the amount of the catalytic metal salt in the composition does not exceed 8 grams per liter and in a made-up bath, does not exceed 2 grams per liter of solution and more preferably ranges between about 0.1 and 1 gram per liter of solution when highly concentrated formulations are made, such as formulations containing 40 to 50 grams per liter, than the pH of the formulation should be above 0.5 and the ratio of the stannous ions to the noble metal ions should be at least 5 to 1.

The particular stannous salt used to formulate the catalyst is likewise not critical and in addition to a stannous halide, other stannous salts are suitable such as stannous nitrate and stannous acetate. As with the salt of the catalytic metal, the stannous halide having an anion common to that of other catalyst constituents is preferred. When a stannous halide is used, a source of halide ions is introduced into the catalyst formulation though this amount by itself does not provide sufficient halide ions for purposes of the preferred embodiment of this invention where excess halide ions are used.

The amount of stannous salt used is not critical provided stannous ions are present in the catalyst formulation in molar excess of the catalytic metal ions. In this respect, as in the prior art, the molar ratio of the stannous ion to the catalytic metal ion may be as low as 2:1, but preferably varies between 10:1 and 40:1 and may be as high as 100:1.

The hydrohalide acids, other than hydroiodic acid, are preferred for purposes of this invention. However, results in terms of stability and catalytic activity with hydrofluoric acid are marginal. Hydrobromic acid is better and hydrochloric acid provides the best result. Accordingly, the term hydrohalide acid as used herein is intended to mean principally hydrochloric acid, but also includes hydrohalide acids other than hydroiodic acid with the realization that these other acids provide

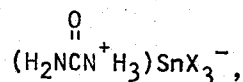
only marginal results. It should be further realized that the term hydrohalide acid means the presence of hydrogen ions and halide ions in solution though the hydrogen ions may be derived from any other acid that does not have an anion detrimental to the catalyst formulation. Thus, sulfuric acid, fluoroboric acid and various organic acids such as maleic acid, as examples, may be used as a source of hydrogen ions with all of the halide ions being supplied by the extraneous source of halide ions. Nitric acid should not be used as it forms insoluble addition products with urea. Likewise, other acids which form insoluble addition products with urea should be avoided.

The amount of acid used may be substantially less than in the commercially acceptable formulations of the prior art. In the prior art, the concentration of the acid had to be sufficiently high so as to provide a catalyst having a pH of less than 1 and typically was so high as to provide a catalyst having a pH below 0. Using hydrochloric acid as an example, as much as 12 moles per liter of solution were used. In accordance with this invention, though such high concentrations of acid can be used, the acid concentration can be reduced to a level whereby the pH of the catalyst is as high as 3.5. Accordingly, for purposes of this invention, that amount of acid is used that results in a solution pH of no greater than 3.5, and in the preferred embodiment of the invention, the acid is used in an amount sufficient to provide a pH ranging between 0.9 and 2.5. It should be noted that though catalysts can be formulated with a pH as high as 3.5, this is principally accomplished when the stannous ion concentration is relatively low and the halide ion concentration is relatively high. Consequently, the stability of catalysts at this high pH is not entirely satisfactory for storage of catalyst for long periods of time.

The addition product of the stannous salt, acid and urea may be obtained by mixing the ingredients together when making the catalyst formulation following the procedures of the aforesaid U.S. Pat. No. 3,011,920 or an addition product of the hydrohalide acid and urea may be formed and then mixed with the stannous salt to form the addition product of the three components. However, if desired, all ingredients may be mixed together in a single container also containing the other components of the catalyst formulation with the addition product believed to be formed in situ. No special reaction conditions such as heating or the like are necessary.

The addition product is believed to be an adduct of urea which utilizes one molecule of the acid and the stannous compound. Consequently, an excess of equimolar amounts of urea is preferred relative to the other constituents, although less than equimolar amounts also provide some benefits. The ratio of urea to the hydrohalide acid may vary between 1:10 and 100:1 but preferably varies between 1:1 and 10:1. From the standpoint of volume only, more urea may be used as the pH of the solution increases and the volume of acid required therefore decreases.

Though not wishing to be bound by theory, it is believed that the addition product used in the formation of the catalyst of this invention conforms to the structure



where X is the halide ion. When an excess of urea is used, which is preferred for purposes of this invention, the uronium ion will drive the reaction for the formation of the addition product to the right, thus preventing dissociation in the catalyst solution. As a result, both the hydrogen halide and the stannous ions are bound up so that the hydrohalide acid will not fume and the stannous ions are prevented from oxidizing to the stannic form.

Decreased oxidation of stannous ion to stannic ion due to the action of urea as a function of time can be seen by reference to FIG. 1 of the drawings which is a graphical representation of stannous content as a function of time for a formulation containing urea (curve A) and one free of urea (curve B). The formulation of examples 1 and 2 below were used to prepare FIG. 1 with air being bubbled through said formulations in an open beaker to accelerate oxidation. Stannous content was determined periodically. As can be seen from the graph, the oxidation of stannous ion is substantially retarded by the presence of the urea. It should be noted that the curves represented herein are illustrative only and only define specifically the systems of examples 1 and 2, other formulations having different but similar curves. For example, stannous ion loss in low acid solution would be reduced even in the absence of urea.

The concentration of urea relative to the acid concentration is more important for lower pH formulations (below about 0.9 for a chloride system) than for higher pH formulations because the tendency of the stannous ion to undergo aerial oxidation is more pronounced in highly acidic solution. FIG. 2 graphically represents the stannous content of a highly acidic catalyst (that of example 1) as a function of the ratio of urea to hydrochloric acid. Measurements were taken after the catalyst had remained standing in an open beaker with air bubbled through for a period of forty hours. It can be seen that the greater the ratio of urea to acid, the greater is the concentration of stannous ion left in the formulation.

Though the aforesaid description has referred only to urea, it should be understood that halides of urea may also be used though these materials are less desirable as they are hygroscopic and therefore present difficulty in terms of raw materials storage. They are, however, included within the scope of the invention and the term urea as used herein refers both to urea and its halides.

From the above description, it can be seen that all of the catalyst components—i.e., the catalytic metal salt, urea, the stannous salt and the acid, may or may not be used in the form of their respective halides though in a preferred embodiment of the invention, they are all halides having a common anion, most preferably chloride. With reference to the definitions set forth above, if all catalyst components were in the form of the halide, the resulting halide concentration, referred to as the maximum component halide ion concentration, would not be sufficiently high to obtain the improvements in the stability and adsorption properties and the retarded precipitation point. Obviously, if one or more of the catalyst components were used in a form other than the halide, then the actual halide ion concentration is still insufficient to obtain the improvements noted above.

In accordance with the preferred embodiments of the

invention described herein, an excess of halide ions is provided in the catalyst formulation, above the maximum component halide ion concentration, by the addition of an extraneous source of halide ion. The amount of the extraneous halide ions added is equal to at least the difference between the actual halide ion concentration and the required total halide ion concentration.

In determining the required total halide ion concentration, different considerations apply dependent upon whether the pH of the catalyst is below or above the precipitation point, the pH at which a precipitate forms, which precipitate is believed to be insoluble hydrolysis products of tin.

With regard first to catalyst formulations having a pH below the precipitation point in the absence of the extraneous halide ions, the total halide ion concentration required is not critical, it being understood that the higher the total halide ion concentration, the greater will be the stability and adsorption properties of the catalyst though the improvements in these properties are sometimes difficult to ascertain, especially with those catalysts having a high hydrogen ion concentration—e.g., a concentration such that the pH of the catalyst is below 0. In general, at a pH below the precipitation point, the total halide ion concentration in accordance with the preferred embodiment described here is at least 0.2 moles in excess of the maximum potential halide ion concentration and preferably, at least 0.5 moles in excess. The maximum concentration is not critical and the total halide ion concentration can be at saturation. Accordingly, halide ion concentration is at least 0.2 moles in excess of the maximum potential halide ion concentration to saturation and preferably is at least 0.5 moles in excess to saturation. The concentration of the extraneous source of halide ions is that amount necessary to increase the actual concentration of the halide ions to the total concentration of halide ions required as described above. Obviously, a greater amount of extraneous halide ions will be required when one or more of the catalyst components such as the catalytic metal salt, the stannous salt or the acid is not in the form of the halide.

With regard to catalyst formulations having a pH above the precipitation point (in the absence of an extraneous source of halide ions), the amount of excess halide ion is more difficult to define as it is dependent upon the pH of the catalyst and the concentration of the stannous ions. The relationship between total halide ion concentration, pH and stannous ion content is depicted in FIGS. 3 and 4 of the drawings for the system palladium chloride (1 gram per liter of solution), urea (50 grams per liter) stannous chloride, hydrochloric acid and lithium chloride as the source of the extraneous ions. It should be understood that other systems are similar to this system though the numerical limitations defining the curves might differ.

In FIG. 3 of the drawings, there is depicted two families of curves. The first family comprise curves, A, B C and D which represent the change in the precipitation point of the catalyst (pH) as a function of total chloride ion concentration for several different stannous ion concentrations. The second family of curves, A', B', C' and D' represent the actual chloride ion concentration derived from the total of the catalyst components—the stannous chloride, palladium chloride and hydrochloric acid, but not the lithium chloride. Curves A and A' are

for a stannous ion content of 0.05 moles per liter of solution, B and B' for 0.13 moles per liter of solution, C and C' for 0.26 moles per liter of solution and D and D' for 0.39 moles per liter of solution. The precipitation point for this catalyst system in the absence of any extraneous halide ions (lithium chloride) is at a pH of about 0.9. As extraneous chloride ions are introduced into the system and the total chloride ion concentration is increased, the precipitation point (pH) is also increased, but not as rapidly for formulations having a low stannous ion concentration (Curve A). Thus, it can be seen that the highest pH (about 3.5) is obtainable only with the lowest concentration of stannous ion and the highest total concentration of chloride ion. As the total chloride ion concentration decreases or the stannous ion concentration increases, the highest possible pH decreases.

The curves of FIG. 3 represent precipitation point. Therefore, the area above any given curve represents a stable catalyst while the area below the curve represents a catalyst containing a precipitate that is of no commercial value.

FIG. 3 may be used to determine the amount of extraneous halide ion required for the catalyst formulation. This is determined from the concentration difference between curves at any given pH and stannous ion concentration. For example, at a pH of 2 and a stannous ion concentration of 0.26 moles per liter of solution (Curves C and C'), the concentration difference between curves C and C' is about 4.5 so that the concentration of extraneous chloride ions required to reach the precipitation point is 4.5 moles per liter of solution. Thus, 4.5 moles of lithium chloride are added to the formulation to provide a total chloride ion concentration of about 5 moles per liter of solution. However, this chloride ion concentration is only sufficient to reach the precipitation point of the catalyst and the total chloride ion concentration should be in excess of this amount to provide a stable catalyst. In general, for this catalyst system and others within the scope of the invention, the total halide ion concentration should be at least about 0.2 moles per liter of solution above the halide ion concentration at the precipitation point of the catalyst and preferably at least above 0.5 moles per liter of solution above that required at the precipitation point. The upper limit is not critical and can be the saturation point of the halide ion in solution. Applying these general guidelines to the specific formulation depicted in FIG. 3, again making reference to the example at a pH of 2 and a stannous ion concentration of 0.26 moles per liter of solution, the total chloride ion concentration at the precipitation point is 5 moles per liter of solution, but to assure the stability, the total chloride ion concentration should be at least 5.2 moles per liter of solution and preferably at least 5.5 moles per liter of solution. Accordingly, the concentration of the extraneous chloride ions—the lithium chloride, added to the formulation should be more than 4.5 moles per liter of solution, preferably should be at least 4.7 moles per liter of solution and more preferably, should be at least 5.0 moles per liter of solution.

With respect to FIG. 3 described above, lithium chloride was selected as the source of the extraneous chloride ion because of its very high solubility in solution. Other halide salts are not as soluble. For example, when sodium chloride is selected as a source of extraneous chloride ion, the solution becomes saturated

when the total concentration is about 6.0 moles per liter. This puts a practical limitation on the maximum pH obtainable as FIG. 3 indicates that when the formulation contains 0.39 moles per liter of solution of stannous ion, the maximum obtainable pH with 4.5 of total chloride ion is about 1.65. When the solution contains only 0.05 moles per liter of solution of stannous ion, the maximum possible pH is about 2.5 with 4.5 total moles of chloride ion.

With regard to the source of the extraneous halide ion, any halide salt having the requisite solubility properties is suitable provided it does not have a cation that would interfere with the functioning of the catalyst. In this respect, illustrative halide salts that are suitable include aluminum chloride, aluminum bromide, magnesium chloride, sodium chloride, sodium bromide, potassium chloride, potassium bromide, calcium chloride, calcium bromide and the like. Lithium halides are preferred because of their solubility and aluminum halides are least preferred because such salts tend to interfere with the functioning of the catalyst.

In FIG. 4 of the drawings, there is graphically presented a family of curves showing the precipitation point of the aforesaid palladium chloride-stannous chloride-urea-hydrochloric acid catalyst system as a function of the stannous ion concentration at different total halide ion concentrations. Again, the source of the extraneous halide concentration necessary to increase the actual halide ion concentration to the total halide ion concentration is lithium chloride. Each curve in the family of curves is numbered and the numbers proceed from 1 through 8. Each number on the curve is the total halide ion concentration for that curve. Each curve represents the precipitation point of the catalyst under consideration and it should be understood that the region to the left of any given curve represents a useable catalyst and the region to the right of any given curve represents a catalyst not having a pH in excess of the precipitation point and one wherein a precipitate has formed.

From FIG. 4, it can be seen that as the total chloride ion concentration increases, as one progresses from Curve No. 1 to Curve No. 8, the maximum possible pH also increases. It can also be seen that the concentration of the stannous ion becomes more important at the higher pH levels. For example, where the total chloride ion concentration is 8 moles per liter of solution, the maximum pH obtainable with 0.4 moles per liter of stannous ion is 2.4 whereas with only 0.5 moles per liter of stannous ion, the maximum pH is in excess of 3.5. Since the curves in FIG. 4 represent precipitation point, a slight excess of total chloride ion concentration beyond that represented in the curve is required to make a catalyst free of precipitate.

It should be noted that at the high pH, the role of the urea is less critical than in the highly acidic compositions. Urea provides some improvement at the higher pH, but the improvement is less dramatic.

Catalysts can be formulated using procedures of the prior art with the extraneous halide ion dissolved in acid solution used to dissolve the other catalyst components, with the addition of urea at any point in the process. A preferred method for formulating a catalyst in accordance with the invention would comprise first preparing a catalyst concentrate using pre-mixed urea-stannous chloride and hydrochloric acid and then diluting the concentrate when ready for use. In this way, the concentrate can be made fairly acidic to insure proper

dissolution of the catalyst components and then the pH can be increased to the extent desired by dilution. The concentrate would be prepared by first dissolving the catalytic metal salt in acid solution, then adding the addition product of stannous chloride, urea and acid and letting the formulation age. During the ageing process, the catalyst will turn from a dark blue to green to brown to brown-black coloration evidencing the formation of the colloid. Following ageing, the catalyst can, if desired, be diluted with a sodium chloride solution whereby the pH is raised and the chloride concentration increased. Where a catalyst having a pH above the precipitation point is desired, the same procedure is involved, but as a final step, some of the acid can be neutralized with a suitable neutralizing agent, preferably a weak base such as sodium bicarbonate,

As also disclosed in the above mentioned U.S. Pat. No. 3,011,920, a stannate such as an alkali metal stannate may also be added to the catalyst composition. The effect of a stannate salt is to improve the properties of the components thereof and obtain quicker adsorption of the catalytic metal on the substrate. The manner in which the stannate achieves this result is not fully understood, but is believed to be due to the presence of stannic (Sn^{+4}) ions in the formulation. Other sources of stannic ions, such as stannic chloride, polystannic acid compounds, and the like may be substituted for the stannate, with similar results.

The invention will be further exemplified by the following illustrative embodiments.

EXAMPLE 1

A 1 percent by weight palladium chloride solution is prepared by adding one gram palladium chloride to 100 milliliters of 0.5N hydrochloric acid. A second solution (containing 27.86g of stannous ions) is added to the first, along with 0.4 g of sodium stannate. To this is added 610 ml of a third solution prepared by mixing 330 ml of 12.4N hydrochloric acid with 350 grams of urea. The mixture thus contains about 1.4 moles of urea per mole of hydrochloric acid. The mixture is stirred, diluted to 1 liter with water and permitted to stand for about 24 hours. The resultant catalyst formulation is of a dark brown coloration. No hydrochloric acid fumes are detectable.

EXAMPLE 2

For purposes of comparison, the formulation of Example 1 above is compared with that of Example 2 of U.S. Pat. No. 3,011,920 which is reproduced below:

Palladium chloride	1 gram per liter
water	600 ml
hydrochloric acid (12N)	300 ml.
sodium stannate	1 1/2 grams
stannous chloride (1)	37 1/2 grams
(1) 23.5 grams per liter of tin	

The above ingredients are mixed together in the order indicated and permitted to stand for 24 hours at about 80°F.

200 ml of each of the above solutions are placed in an open beaker and air is bubbled through each solution at a rate of 10 cubic feet per hour. Periodically, a small sample of each solution is removed and titrated for tin. The results are graphically illustrated in FIG. 1 of the drawing which is a plot of stannous content versus time as described above. As can be seen from the drawing, the formulation of Example 1 set forth herein lasted for a period in excess of 200 hours, at which time, the test was discontinued while the formulation of Example 2 of U.S. Pat. No. 3,011,920 became unstable within about 48 hours when about one-half gram of stannous ion was left in solution.

As noted above, the use of excess halide ions permits pH stable catalyst solutions having lower stannous concentrations than previously possible. The urea addition product is also effective in stabilizing such solutions, as shown by the following example:

EXAMPLE 3

a. The procedure of example 1 is repeated with reduction in the amount of stannous chloride to 32 grams per liter of solution (19.2 grams per liter of tin). Upon initial titration, there was found to be 19.0 grams per liter of stannous ion and after 45 hours of aeration, there was found to be 11.3 grams per liter of solution.

b. The procedure of example 1 was repeated, but the amount of stannous chloride was reduced to 6 1/2 grams per liter (4.9 grams per liter of tin). The catalyst became unstable and a precipitate formed within about ten hours.

c. The procedure of example 1 was repeated but the stannous chloride content was reduced to about 3 grams per liter (1.8 grams per liter of tin). The catalyst became unstable after about eight hours.

d. The procedure of example 2 was repeated, but the stannous chloride content was reduced to about 15 grams (9.0 grams per liter tin). The catalyst became unstable and a precipitate formed in about 6 hours.

e. The procedure of example 2 was repeated but the stannous chloride content was reduced to 6 1/2 grams per liter (4.9 grams per liter of tin). The catalyst became unstable within about two hours after make-up.

f. The procedure of example 2 was repeated but the stannous chloride was reduced to 3 grams per liter (1.8 grams per liter of tin). The catalyst became unstable almost immediately after make-up.

It has been found that it is preferable to use the urea in relatively large molar excess of the hydrohalide acid. The reason for this is believed to be that it prevents dissociation of the addition product. The advantages are illustrated in the following example.

EXAMPLE 4

Six catalyst formulations were prepared according to the procedure of example 1, except that the urea content (and correspondingly the ratio of urea to hydrochloric acid) was varied so as to show the effect of urea upon solution stability. The molar ratio of urea to hydrochloric acid, and stannous content variation upon exposure to air is set forth in the following table:

Ratio Urea:HCl	0 hours	Stannous content 20 hours	content 40 hours	(grams/liter) 60 hours	140 hours
0:1	24.0	12.0	3.5	unstable ⁽¹⁾	unstable
0.5:1	20.4	13.5	8.6	3.2	unstable
1:1	19.6	14.0	11.2	9.4	unstable
2:1	19.9	14.2	14.2	12.3	3.8
3:1	20.8	17.1	16.1	14.2	10.4
4:1	20.8	17.1	17.1	16.1	10.4

⁽¹⁾Unstable—The catalyst becomes unstable when the stannous ion content drops below 1 gram per liter.

To illustrate the relationship between the ratio of urea to hydrohalide acid and stannous content, in the above table, ratio versus stannous content at 40 hours is plotted and represented in FIG. 4 as discussed above. As can be seen from the drawing, the higher the ratio of the urea to the hydrochloric acid, the greater the stannous content is after 40 hours of solution aeration.

The above, it can be seen that best results are at the higher ratios of urea to hydrochloric acid, though as the urea content exceeds 3 moles per mole of hydrochloric acid, little or no improvement is obtained.

Example 5

Palladium chloride	0.25 grams per liter
Stannous chloride	3.2 grams per liter
hydrochloric acid (12N)	2.5 ml
sodium chloride	250 grams per liter
sodium stannate	0.5 grams per liter
urea	50 grams per liter
water	to 1 liter of solution

The above solution had a pH of 1.2. It was stable for in excess of 150 hours with exposure to air as in the manner of example 1. Comparison of this example with example 3, paragraph C, above shows the substantially improved results using the higher pH.

A major advantage of a dilute solution such as that of this example 5 is economic, especially for plating on plastics where "drag-out" is a problem. Also, such solutions can be replenished with fairly concentrated solutions without substantial volume growth.

The formulations of this invention find substantially the same use as the prior art catalytic formulations, such as those disclosed in the aforesaid U.S. Pat. No. 3,011,920. As a specific example of a complete processing procedure according to this invention, the following is given for a copper-clad plastic laminate substrate provided with through-holes at desired locations:

EXAMPLE 6

1. Pre-cleaning the copper substrate:

- Clean the substrate by immersion in hot alkaline cleaner, and rinse in clean water.
- Pickle in an acid bath with an etchant for copper, for example, a cupric chloride-hydrochloric acid bath, and rinse.
- Dip in a 10% volume hydrochloric acid solution to remove residues, and rinse.

2. Catalysis:

Immerse the clean substrate for 30 seconds or more in the catalyst solution according to example 1 which catalyzes both the copper surfaces and the plastic surface exposed in the through-hole walls. Rinse.

3. Acceleration (optional):

Immerse in an acidic accelerating solution, for example, 10% fluoboric acid solution, for 1 minute or more, and rinse.

4. Metal Deposition:

Immerse the catalyzed surface in the desired metal deposition solution, for example, a copper bath such as that of example 1 of U.S. Pat. No. 3,329,512 included

herein by reference, for a sufficient time to build-up the desired thickness of metallic coating. Rinse thoroughly and dry.

5. Electroplating:

Immerse the coated substrate in a 10% solution of hydrochloric acid to assure a clean copper coating, rinse and electroplate copper over the electroless coating until a desired thickness is obtained.

With this process, strong uniform coatings of conductive metal are provided on the substrate on both the plastic surface exposed in the through-holes and on the metal surfaces without the necessity of removing the metal coating from the cladding prior to electroplating.

EXAMPLE 7

The procedure of example 6 is repeated substituting the catalytic formulation of example 5 for that of example 1 with similar results.

For deposition onto unclad, non-metallic surfaces, the following procedure can be employed.

EXAMPLE 8

1. Catalysis:

Immerse the substrate for 30 seconds or longer in the catalytic formulation of example 1 above and rinse.

2. Acceleration:

Immerse the catalyzed substrate in an alkaline accelerator, for example 5% sodium carbonate for 1 minute or more, and rinse.

3. Metal Deposition:

Immerse the catalyzed substrate in the desired metal deposition solution, for example, the formulation of example 1 of U.S. Pat. No. 3,424,597 incorporated herein by reference for a sufficient time to build-up the desired thickness of metallic coating. Rinse thoroughly and dry.

EXAMPLES 9-26

Catalyst solutions are made up containing 0.25 g/l palladium chloride, 10 g/l stannous chloride and 0.5 g/l stannic chloride, and the amounts of the other materials listed below, in enough water to make 1 liter. Acrylonitrile-butadiene-styrene plates are scrubbed, rinsed, cleaned with a detergent to remove grease and oil, rinsed, immersed in 10% by volume hydrochloric acid, immersed directly in the various catalyst compositions for thirty seconds, rinsed, immersed for one minute in a solution of Accelerator 19, available from Shipley Company, rinsed, immersed in an electroless plating bath as in example 6 and subjected to a final rinse.

The coatings obtained are visually evaluated for completeness, depth, and uniformity of coverage with the results reported below:

Example Number	Urea Concentration (moles)	Chloride Salt Concentration (grams)	HCl Concn. (Norm)	Result
9	0.0	250 NaCl	0.1	Excell.
10	0.3	250 "	0.1	Excell.
11	0.25	250 "	0.1	Excell.
12	1.0	250 "	0.1	Excell.
13	3.5	25 "	2	Excell.
14	3.5	80 "	2	Excell.
15	3.5	200 "	2	Excell.

-Continued

Example Number	Urea Concentration (moles)	Chloride Salt Concentration (grams)	HCl Concen. (Norm)	Result
16	0.1	280 "	.03	Excell.
17	0.2	280 "	.03	Excell.
18	1.0	280 "	.03	Fair
19	2	40 "	4	Excell.
20	4	40 "	4	Excell.
21	6	40 "	4	Excell.
22	8	40 "	4	Fair
23	0.1	318 KCl	.1	Good
24	6	100 KCl	4	Excell.
25	0.1	236 NH ₄ Cl	.1	Good
26	0.1	192 AlCl ₃	.1	Fair

EXAMPLES 27 through 30

These examples illustrate the preparation of the catalyst used for the derivation of FIGS. 3 and 4 of the drawings. Four stock solutions were prepared and la-

Each of the above formulations was divided into ten equal portions (100 ml each) and lithium chloride added to each to bring the total concentration to a desired amount. Each of the so formed catalyst were then titrated with sodium bicarbonate to neutralize the acid to a point where turbidity was seen. This was considered to be the precipitation point. The chloride introduced from each of the hydrochloric acid, the stannous chloride and the lithium chloride as well as total chloride and precipitation point are set forth in the following table. With reference to the table, it should be understood that the chloride concentrations are set forth in moles per 100 ml of solution though in FIG. 3 of the drawings, this has been converted to moles per liter. Moreover, with regard to FIG. 3, the first point in the curve represents a known precipitation point for a catalyst having a pH of 0.9 and was derived from formulation having a higher initial concentration of hydrochloric acid.

Solution Identif.	(Cl ⁻) _{HCl}	(Cl ⁻) _{SnCl₂}	(Cl ⁻) _{LiCl}	(Cl ⁻) _T	Precipitation Point (pH)
1-1	.100	.010	0	.110	1.3
1-2	.100	.010	.090	.200	1.7
1-3	.100	.010	.190	.300	1.9
1-4	.100	.010	.290	.400	2.3
1-5	.100	.010	.390	.500	2.7
1-6	.100	.010	.490	.600	3.0
1-7	.100	.010	.590	.700	3.3
1-8	.100	.010	.690	.800	3.5
2-1	.100	.026	0	.126	1.1
1-2	.100	.026	.074	.200	1.4
2-3	.100	.026	.174	.200	1.4
2-4	.100	.026	.274	.400	2.1
2-5	.100	.026	.374	.500	2.3
2-6	.100	.026	.474	.600	2.5
2-7	.100	.026	.574	.700	2.8
2-8	.100	.026	.674	.800	3.1
3-1	.100	.052	0	.152	1.1
3-2	.100	.052	.048	.200	1.3
3-3	.100	.052	.148	.300	1.6
3-4	.100	.052	.248	.400	1.9
3-5	.100	.052	.348	.500	2.0
3-6	.100	.052	.448	.600	2.3
3-7	.100	.052	.548	.700	2.5
3-8	.100	.052	.648	.800	2.7
4-1	.100	.078	0	.178	1.2
4-2	.100	.078	.022	.200	1.2
4-3	.100	.078	.122	.300	1.2
4-4	.100	.078	.222	.400	1.6
4-5	.100	.078	.322	.500	1.7
4-6	.100	.078	.422	.600	1.9
4-7	.100	.078	.522	.700	2.0
4-8	.100	.078	.622	.800	2.3

belled sequentially 1 to 4. The solutions had compositions as follows:

Solution No.	1	2	3	4
palladium chloride(gm)	1	1	1	1
stannous chloride (gm)	10	25	50	75
Urea (gm)	50	50	50	50
Hydrochloric acid(37%-ml)	80.6	80.6	80.6	80.6
Water		to 1 liter		

The formulations were prepared by dissolving the palladium chloride in the hydrochloric acid and half the water. Stannous chloride was then added very slowly with stirring and the resulting solution was permitted to age until a dark brown coloration was obtained. The remaining water was then added. The pH of the resulting solution was 0.

The curves of FIG. 3 are approximations as the precipitation point was observed visually and subject to experimental error. The explanation of the results of this series of experiments is set forth above and will not be repeated here.

Various of the above formulations were again prepared though the total chloride ion concentration was increased by 0.1 moles per 100 milliliters so that the total chloride ion concentration was in excess of the chloride ion concentration and the precipitation point. Stability of these formulations was determined by purging a portion of the formulation into a petri dish and leaving the petri dish exposed to air for a prolonged period of time. In this way, the catalyst formulation had a relatively large exposed surface area. The catalyst was left exposed to air in this manner until such time

as a precipitate formed. The results obtained are set forth in the following table:

Solution Identif.	Time to Precipitate (hrs)	Silver Film
1-1	170	No
1-4	50	No
1-8	5	Yes
2-1	200	No
2-4	200	No
2-8	25	No
3-1	200	No
3-4	165	No
3-8	15	No
4-1	200	No
4-4	200	No
4-8	200	No

of the volume of water. The urea was then mixed with stannous chloride and added in an initial amount such that there was an excess and the balance added slowly with stirring. The solutions were then permitted to age until a brown coloration was obtained. The solutions were then split into three equal 1 liter portions and additional sodium chloride in a given amount was then added to each of the separate solutions. The catalysts were then titrated with sodium bicarbonate to increase the pH and determine the precipitation point of the catalyst. The following table sets forth solution identification, chloride content from each of the hydrochloric acid, stannous chloride and sodium chloride, the total chloride content and the precipitation points of the catalyst.

Solution Identif.	(Cl ⁻) _{HCl}	(Cl ⁻) _{SnCl₂}	(Cl ⁻) _{NaCl₂}	(Cl ⁻) _T	Precipitation Point (pH)
31-1	0.1	.10	1.00	1.20	1.4
31-2	0.1	.10	1.80	2.00	1.7
31-3	0.1	.10	3.80	4.00	2.3
32-1	0.1	.26	1.00	1.36	1.3
32-2	0.1	.26	1.64	2.00	1.6
32-3	0.1	.52	3.64	4.00	2.1
33-1	0.1	.52	1.00	1.62	1.3
33-2	0.1	.52	1.38	2.00	1.5
33-3	0.1	.52	3.38	4.00	1.9
34-1	0.1	.78	1.00	1.88	0.9
34-2	0.1	.78	1.12	2.00	0.9
34-3	0.1	.78	3.12	4.00	1.3

The catalysts having solution identification numbers beginning with 1 were less stable than the other catalysts because of the low stannous ion concentration. Only one of the catalysts exhibited a silver film characteristic of a catalyst left exposed to air for a long period of time.

To demonstrate the functional properties of the catalyst of these examples, the plating sequence of Example 6 above was adopted for the plating of an epoxy copper clad circuit board base material provided with a random array of through-holes. The catalyst used were those described in the immediately preceding table. Following the process of Example 6, each of the tested catalysts formulations provided a strong uniform coating of conductive metal on the plastic surface exposed in the through-holes and on the backside of the circuit board base material as well as on the copper clad. There was no necessity for removal of the metal coating over the copper clad material prior to electroplating as the bond between the copper clad and the electroless copper deposit was quite strong.

It should be noted that the results obtained here are quite similar to the results obtained with formulations free of urea as at the relatively high pH used, the function of the urea is of lesser importance.

Examples 31 to 34

Solution No.	31	32	33	34
Palladium chloride (gm)	3	3	3	3
Stannous chloride (gm)	30	75	150	225
Hydrochloric acid(12N ml)	24.2	24.2	24.2	24.2
Urea	100	100	100	100
Sodium chloride (gm)	174	174	174	174
Water	to 3 liters			

The above formulations were prepared by dissolving the palladium chloride and sodium chloride in one-half

From the above, it can be seen that the results obtained are similar to those obtained in Examples 1 through 4. Moreover, each of the catalysts set forth in the immediately preceding table were highly effective in catalyzing a substrate in the metallization process described above.

In the aforesaid Examples 31 through 34, the maximum concentration of extraneous chloride ion is about 4.5 moles per liter of solution because of the limited solubility of sodium chloride. Accordingly, using sodium chloride, the maximum possible pH obtainable with 10 grams of stannous chloride per liter of solution is about 2.5.

As with the aforesaid examples, the presence of urea makes a less dramatic effect on the stability of the formulation because of the relatively high pH employed.

The following are examples of formulations within the scope of the invention. All are capable of catalyzing a substrate following the procedure described above.

Example 35

Palladium nitrate (gm)	1
Stannous nitrate (gm)	25
Fluoroboric acid (48%-ml)	50
Calcium chloride (gm)	100
Urea (gm)	200
Water	to 1 liter

Example 36

Palladium sulfate (gm)	1
Stannous Sulfate (gm)	25
Sulfuric acid (ml)	20
Calcium bromide (gm)	100
Urea	200
Water	to 1 liter

Example 37

Palladium chloride (gm)	0.5
Stannous fluoborate(gm)	50
Fluoroboric acid (48%-ml)	50
Calcium chloride (gm)	200

-Continued

Urea	100
Water to 1 liter	
Example 38	
Palladium bromide (gm)	0.50
Stannous bromide (gm)	25
Hydrobromic acid (48%-ml)	100
Sodium bromide (gm)	150
Urea	50
Water to 1 liter	
Example 39	
Palladium bromide (gm)	0.50
Stannous sulphate (gm)	50
Fluoroboric acid (48%-ml)	35
Magnesium bromide	250
Urea	250
Water to 1 liter	
Example 40	
Gold chloride (gm)	1
Stannous chloride (gm)	25
Hydrochloric acid (37%-ml)	10
Sodium chloride (gm)	200
Urea	100
Water to 1 liter	
Example 41	
Platinum chloride (gm)	1
Stannous chloride (gm)	25
Hydrochloric acid (37%-ml)	10
Sodium chloride (gm)	200
Urea	100
Water to 1 liter	
Example 42	
Rhodium sulfate (gm)	1
Stannous sulfate (gm)	25
Sulfuric acid (96% ml)	3
Sodium chloride (gm)	200
Urea	100
Water to 1 liter	
Example 43	
Palladium chloride (gm)	0.5
Platinum chloride (gm)	0.5
Stannous chloride (gm)	25
Hydrochloric acid (37%ml)	25
Sodium chloride (gm)	100
Urea	250
Water to 1 liter	

EXAMPLES 44 to 46

The following examples illustrate a catalyst with a very low stannous ion concentration:

	44	45	46
palladium chloride (gm)	0.25	0.25	0.25
Stannous chloride	3.2	3.2	3.2
Hydrochloric acid (37% ml)	2.0	10	80
Sodium chloride (gm)	200	200	200
Urea	100	100	100
Water	to a liter		

All of the above were made according to the process of Example 37. The formulation of Example 44 was stable in a petri dish exposed to air for a period of 105 hours, the formulations of Example 45 was stable for period of 83 hours and that of Example 46 for a period of 72 hours.

While the particular embodiments of the present invention have been shown and described, it will be obvious to those skilled in the art that changes and modifications may be made without departing from the invention in its broader aspects. Therefore, it is intended that the specification be interpreted as illustrative only, and not in any limiting sense.

We claim:

1. A catalyst composition for catalyzing a substrate prior to electroless metal deposition thereon, said catalyst composition comprising the product resulting from

the admixture of an acid soluble salt of a catalytic metal selected from the group consisting of silver, gold and the platinum family metals, a solution soluble stannous salt in molar excess of the catalytic metal salt, a hydrohalide acid sufficient to provide a pH less than 1 and urea in an amount such that the molar ratio of the urea to the hydrohalide acid exceeds 1 to 10.

2. The composition of claim 1 where the catalytic metal salt is a member of the platinum family of metals.

3. The composition of claim 2 where the catalytic metal salt does not exceed 8 grams per liter of solution.

4. The composition of claim 1 where the catalytic metal salt varies between 0.1 and 5 grams per liter of solution.

5. The composition of claim 4 where the acid is selected from the group consisting of hydrochloric acid and hydrobromic acid.

6. The composition of claim 4 where the acid is hydrochloric acid.

7. The composition of claim 6 where the catalytic metal salt is a palladium salt.

8. The composition of claim 6 where the catalytic metal salt is palladium chloride.

9. The composition of claim 8 also containing an alkali stannate salt.

10. The composition of claim 1 where the molar ratio of the stannous salt to the catalytic metal salt varies between 2:1 and 100:1.

11. The composition of claim 10 where the ratio varies between 10:1 and 40:1.

12. The composition of claim 1 where the molar ratio of urea to hydrohalide acid varies between 1:10 and 100:1.

13. The composition of claim 12 where the ratio varies between 1:1 and 10:1.

14. A catalyst composition for catalyzing a substrate prior to electroless metal deposition thereon, said catalyst comprising the product of admixture of palladium chloride, stannous chloride in molar excess of the palladium chloride, hydrochloric acid sufficient to provide a pH less than 1 and urea in an amount such that the molar ratio of urea to hydrochloric acid exceeds 1 to 10.

15. The composition of claim 14 where the palladium chloride does not exceed 8 grams per liter of solution.

16. The composition of claim 14 where the palladium chloride varies between 0.1 and 5 grams per liter of solution.

17. The composition of claim 14 also containing an alkali stannate salt.

18. The composition of claim 14 where the molar ratio of the stannous chloride to palladium chloride varies between 2:1 and 100:1.

19. The composition of claim 18 where the ratio varies between 10:1 and 40:1.

20. The composition of claim 14 where the molar ratio of urea to hydrochloric acid varies between 1:10 and 100:1.

21. The composition of claim 20 where the molar ratio varies between 1:1 and 10:1.

22. A catalyst composition for catalyzing a substrate prior to electroless metal deposition thereon, said composition comprising the product resulting from the admixture of (1) a salt of a catalytic metal selected from the group of gold, silver and the platinum family metal salts, (2) the addition product formed from a stannous salt in an amount such that the stannous ion concentra-

tion is in molar excess of the catalytic metal ion concentration, an acid in an amount sufficient to provide a pH less than about 3.5 and urea in an amount such that the molar ratio of urea to the acid exceeds 1 to 10, and (3) a halide salt in an amount such that the total halide ion concentration at a pH below the precipitation point of the catalyst is at least 0.2 moles per liter in excess of the concentration of halide ions provided by all other components and at a pH at or above the precipitation point is at least sufficient to prevent the formation of a precipitate.

23. The composition of claim 22 where the pH is below the precipitation point and the total halide ion concentration is from 0.2 moles in excess of the concentration of halide ions provided by all other catalyst components to saturation.

24. The composition of claim 23 where the total halide ion concentration is from 0.5 moles in excess of the concentration of halide ions from all other catalyst components to saturation.

25. The formulation of claim 22 where the pH is at or above the precipitation point and the total halide ion concentration varies from at least 0.2 moles in excess of that required to prevent formation of a precipitate to saturation.

26. The composition of claim 25 where the total halide ion concentration varies from at least 0.5 moles in excess of that required to prevent formation of a precipitate to saturation.

27. The composition of claim 22 where all halide ions are chloride ions.

28. The composition of claim 27 where the pH varies between about 0.9 and 3.5.

29. The composition of claim 27 where the pH varies between about 0.9 and 2.5.

30. The composition of claim 22 where the molar ratio of the stannous ion from the stannous salt to the catalytic metal ion from the salt of the catalytic metal varies between 2:1 and 100:1.

31. The composition of claim 30 where the ratio varies between about 10:1 and 40:1.

32. The formulation of claim 22 where the catalytic metal salt is palladium chloride.

33. The composition of claim 22 where the molar ratio of urea to acid varies between 1:10 and 100:1.

34. The composition of claim 33 where the ratio varies between 1:1 and 10:1.

35. A catalyst composition for catalyzing a substrate prior to electroless metal deposition thereon, said composition comprising the product of admixture of (1) a catalytic metal halide salt selected from the group of a gold halide, a silver halide and a platinum family metal halide, the concentration of said catalytic metal halide not exceeding 50 grams per liter of solution (2) the addition product formed from a stannous halide in an amount such that the stannous ion concentration is in molar excess of the catalytic metal ion concentration, the molar ratio of said stannous ion to said catalytic metal ion varying between 2:1 and 100:1, a hydrohalide acid in an amount sufficient to provide a formulation having pH less than about 3.5 and urea in an amount such that the molar ratio of urea to acid exceeds 1:10 and (3) a halide salt in an amount such that the total halide ion concentration at a pH below the precipitation point of the catalyst is at least 0.2 moles per liter in excess of the concentration of halide ions provided by all other catalyst components and at a pH at or

above the precipitation point of the catalyst, is at least sufficient to prevent formation of a precipitate.

36. The composition of claim 35 where all of the halide ions are chloride ions.

37. The composition of claim 36 where the pH is below the precipitation point and the total chloride ion concentration is from 0.2 moles in excess of the concentration of chloride ions provided by all other catalyst components to saturation.

38. The composition of claim 37 where the total chloride ion concentration is from 0.5 moles in excess of the concentration of chloride ions provided from all other catalyst components to saturation.

39. The composition of claim 36 where the pH is at or above the precipitation point of the catalyst and the total chloride ion concentration varies from at least 0.2 moles in excess of that required to prevent formation of a precipitate to saturation.

40. The composition of claim 39 where the total chloride ion concentration varies from at least 0.5 moles in excess of that required to prevent formation of a precipitate to saturation.

41. The composition of claim 36 where the pH varies between about 0.9 and 3.5.

42. The composition of claim 36 where the pH varies between about 0.9 and 2.5.

43. The composition of claim 36 where the molar ratio of the stannous ion to catalytic metal ions varies between about 10:1 and 40:1.

44. The composition of claim 43 where the catalytic metal salt is palladium chloride.

45. The composition of claim 36 where the molar ratio of urea to hydrochloric acid varies between 1:10 and 100:1.

46. The composition of claim 45 where the ratio varies between 1:1 and 10:1.

47. A catalyst composition for catalyzing a substrate prior to electroless metal deposition thereon, said composition comprising the product of admixture of (1) palladium chloride in an amount not exceeding 50 grams per liter of solution, (2) the addition product formed from stannous chloride in an amount such that the stannous ion is in molar excess of the palladium ion concentration, the molar ratio of said stannous ion to said palladium ion varying between 2:1 and 100:1, hydrochloric acid in an amount sufficient to provide a composition having a pH less than about 3.5 and urea in an amount such that the ratio of urea to acid exceeds 1:10 and (3) a chloride salt in an amount such that the total chloride ion concentration at a pH below the precipitation point of the catalyst is at least 0.2 moles per liter in excess of the concentration of the balance of the chloride ions provided by all other catalyst components and at a pH at or above the precipitation point of the catalyst, is at least sufficient to prevent the formation of a precipitate.

48. The composition of claim 47 where the pH is below the precipitation point and the total chloride ion concentration is from 0.2 moles in excess of the concentration of chloride ions provided by all other catalyst components to saturation.

49. The composition of claim 48 where the total chloride ion concentration is from 0.5 moles in excess of the concentration of chloride ions from all other catalyst components to saturation.

50. The composition of claim 47 where the pH is at or above the precipitation point and the total chloride

ion concentration varies from at least 0.2 moles in excess of that required to prevent formation of a precipitate to saturation.

51. The composition of claim 50 where the total chloride ion concentration varies from at least 0.5 moles in excess of that required to prevent formation of a precipitate to saturation.

52. The composition of claim 47 where the pH varies between about 0.9 and 3.5.

53. The composition of claim 47 where the pH varies between about 0.9 and 2.5.

54. The composition of claim 47 where the molar ratio of the stannous ions to the palladium ions varies between about 10:1 and 40:1.

55. The composition of claim 47 where the chloride salt is selected from the group consisting of aluminum chloride, magnesium chloride, sodium chloride, potassium chloride, calcium chloride and lithium chloride.

56. The composition of claim 55 where the chloride salt is sodium chloride.

57. The process for stabilizing a catalyst for catalyzing a substrate prior to electroless metal deposition, said catalyst comprising the product of (1) catalytic metal ions, (2) stannous ions in an amount in molar excess of said catalytic metal ions, (3) halide ions and (4) hydrogen ions in an amount sufficient to provide a formulation having a pH less than about 3.5, said process comprising adding urea to said catalyst composition, the concentration of urea being such that the molar ratio of the urea to the hydrogen ions is at least 1 to 10.

58. The process of claim 57 where the catalytic metal ions are palladium ions in a concentration not exceeding 8 grams per liter.

59. The process of claim 58 where the stannous ions are derived from stannous chloride and the molar ratio of stannous ions to palladium ions varies between 2:1 and 100:1.

60. The process of claim 59 where the ratio varies between 10:1 and 40:1.

61. The process of claim 57 where the hydrogen ions are derived from hydrochloric acid.

62. The process of claim 61 where the pH varies between about 0.9 and 3.5.

63. The process of claim 61 where the pH varies between about 0.9 and 2.5.

64. The process of claim 61 where the pH is below the precipitation point of the catalyst and the total chloride ion concentration is from 0.2 moles in excess of the concentration of chloride ions provided by all other catalyst components to saturation.

65. The process of claim 64 where the total chloride ion concentration is from 0.5 moles in excess of the concentration of chloride ions provided by all other catalyst components to saturation.

66. The process of claim 63 where the total chloride ion concentration is at least 0.2 moles in excess of that required to prevent the formation of a precipitate to saturation.

67. The composition of claim 63 where the total chloride ion concentration is at least 0.5 moles in excess of that required to prevent formation of a precipitate to saturation.

68. The process of claim 57 where the concentration of urea is such that the molar ratio of urea to acid varies between 1:1 and 10:1.

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