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3,532,518

COLLOIDAL METAL ACTIVATING SOLUTIONS FOR USE IN CHEMICALLY PLATING NON- CONDUCTORS, AND PROCESS OF PREPAR- ING SUCH SOLUTIONS

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9 Claims

ABSTRACT OF THE DISCLOSURE

Tin-palladium sols for activating nonconductive sub-
strates for the chemical plating and subsequent electro-
plating of a metal on the substrate, and the process of
preparing such sols. The preparation of the sols is char-
acterized by a two-step process involving first the reduc-
tion of a palladium salt to palladium metal in colloidal
form and then stabilization of the colloidal palladium by
the addition of excess stannous salts forming protective
colloids about the palladium metal particles, whereby the
resulting sols exhibit improved activating properties in
the plating cycle.

The present invention is directed to improvements in
solutions for activating non-conductive substrate sur-
faces in processes involving the deposition thereon of a
plating metal by chemical action, and to improvements
in the method of preparing such activating solutions, as
well as in the method of their use in a complete chemical
plating process.

The invention is particularly concerned with the pre-
paration of catalyst metals in the form of aqueous disper-
soids or hydrosols in which catalyst metal particles of
colloidal or semi-colloidal nature are dispersed in aqueous
solution.

For chemical plating of substrates, especially in the
plating of non-conductive substrates, it has been known
for some time that chemically plated metal deposits of
suitable thickness and adequate bonding strength are
commercially practical only if the substrate surface is
properly sensitized and/or activated prior to the chemical
deposition. A common method of activating the substrate
surface to be plated involves contacting the substrate with
a solution of the catalytic or activating metal in ionic
condition and, in a separate step, reducing the metal in
situ on the treated substrate surface by contacting the
latter with a suitable reducing agent. This procedure is
employed successfully in many plating-on-plastic applica-
tions. It is subject to a disadvantage that, in general, it
requires reracking the articles being plated to avoid con-
tamination through drag-in from preceding steps and
rapid deterioration of the plating bath. An alternative
activating method is also known which largely avoids this
difficulty and which affords the added advantage of
reducing the number of steps from a two-step method
to a single step process of activating. In this known
method, the substrate surface is contacted directly with
a solution in which the catalyst metal is already in re-
duced, metallic state in the form of fine colloidal or at
least semi-colloidal particles. The one-step activating so-
lution has accordingly been preferred in many applica-
tions, but the system is not without some difficulties. One
of these has been that of producing hydrosols of the cata-
lytic metal which are stable and consistently and re-
liably operative. Slight variation in conditions of prepa-
ration have a major effect on the character of the hy-
drosol and its effectiveness as an activating solution.

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It is accordingly one of the principle objects of this
invention to provide a procedure for preparing hydrosols
of catalytic metals which insures the operability of such
sols in activating nonconductive substrate surfaces for
chemical plating. It is also a purpose of the invention to
provide a procedure for preparing these sols which is
readily modified to control the aggressiveness of their
activating effect, whereby to vary the activation to suit
different chemical plating requirements or purposes.

In furtherance of this general objective of the inven-
tion, it is a purpose of the invention to provide a com-
mercially practical method of controlling the nature of
the resulting hydrosol to insure that the colloidal or
semicolloidal catalyst metal particles thereof are excep-
tionally uniform in physical size, that the particle size
distribution is held within relatively narrow limits, and
that the shape of the particles is predominantly uniform
and of a form particularly effective for chemical plating
uses.

A further objective of the invention is to teach a pre-
paration method for obtaining activator sols of catalytic
metals which are operative immediately upon being
formulated and which do not, therefore, require periods of
aging or storing to render them operative.

The invention also comprehends the use of activator
solutions prepared in accordance with the teaching herein
in an overall combination of operating steps constituting
a complete chemical plating system, which combination
provides much improved results in the metal deposit
finally obtained on a substrate.

It is known, of course, that various metals exhibit
catalytic properties useful in chemical plating, including
the precious metals gold, silver, members of the platinum
family, as well as certain less precious members of the
group consisting of cobalt, nickel, copper and iron. Pal-
ladium has been found generally to be the most satisfac-
tory of these catalyst metals for the activation of non-
conductive substrates, particularly plastic substrates. This
applies both to plastic articles whose surfaces are to be
covered with a metal finish for decorative or protective
purposes, as well as to substrates such as printed circuit-
boards where the plated deposit is intended to afford
conductive path in electronic circuits.

The principles of the invention herein disclosed are
applicable in general to the preparation of activator
metal sols, but more especially are intended for the pre-
paration of activator metal sols in which palladium is the
catalyst metal employed. Accordingly, the description
which follows is directed more particularly to the details
of preparing and using palladium as the activating metal.

In brief, that aspect of this invention which relates
to the preparation of activator metal sols consists of
certain operating steps performed in a particular order
and under prescribed conditions. Speaking generally, the
preparation of the palladium sols comprises first dis-
solving an appropriate amount of a suitable palladium
salt, such as palladium chloride, in acid solution so that
all of the palladium goes into solution. To this is then
added a reducing agent such as stannous chloride; but it
is an important feature of the invention that only an
equivalent amount of reducer be added, that is just
enough to reduce the palladium from Pd^{+2} to Pd^0 . After
the reducer is added to the palladium chloride solution,
the admixture is thoroughly mixed for a period of time
which is closely controlled and which has significant
effect upon the final particle size, size distribution and
shape in the resulting sol. Upon completion of this sec-
ond step a suitable protective colloid former is mixed
with the balance of the acid needed to give a suitably
stable, low pH system and to this the first solution is
then added with mixing. When these solutions are thor-
oughly mixed, the resultant activator sol is immediately

ready for use in treating the surface of a nonconductor for chemical plating. Stannous chloride is a preferred reducing agent in this preparation since it may also serve, when an excess is added, as the protective colloid former. It is important however that the excess beyond that needed for reducing the palladium not be added until reduction has been completed and colloidal particles of desired form have been obtained.

The procedure outlined above can be, and ordinarily is, carried out at ambient room temperatures. Under certain circumstances which will be discussed more fully hereinafter, the temperatures employed in preparing the activator may be increased to produce certain desired changes in the sols where they are to be used for specific purposes as, for example, for through-hole plating in contrast to straight plating-on-plastic operations.

The activator sols prepared in accordance with the invention are particularly suited for use in the chemical deposition of nickel and copper. Using the sols of the invention, the chemical plating step is rendered quite flexible, i.e. not critical or requiring close control of operating temperature, solution concentrations, etc. Excellent economy of the plating process is also afforded by reason of the fact that greater selectivity of the system is achieved, largely confining the plating metal deposits to those areas that have been treated in the activator solution while suppressing the formation of deposits on tank walls, plating racks and all other parts with which the plating solution comes in contact, but which have not been activated.

The activator sols of the invention are found to be effective in the pretreatment of a wide variety of plastic substrates for chemical plating, including ABS, polysulfones, polypropylenes, polystyrenes, epoxys, phenolics, acrylics, and the like.

PREPARATION OF ACTIVATOR SOLS

This aspect of the invention is illustrated by the following specific example of the preparation of a colloidal, or mixed colloidal-complexed, palladium activator sol. In the description which follows, the sequence of operating steps is important, as well as relative proportions of components employed within those steps, and as will be made more apparent hereinafter, so are the time and temperature conditions prevailing.

EXAMPLE I

An activator sol is prepared by first dissolving 2 grams of palladium chloride (60% Pd) in 200 mls. of concentrated (37%) hydrochloric acid and 400 mls. of de-ionized water. The solution is stirred until the palladium chloride is completely dissolved which normally is effected in about 10-15 minutes. The step is carried out at ambient room temperature, as are all others to follow in this example.

To this palladium chloride solution there is then added 4.0 grams of anhydrous stannous chloride. The resulting mixture is stirred for 12 minutes, during which time the color of the solution changes from initial dark green to dark olive brown.

A separate solution is prepared containing 96 grams of anhydrous stannous chloride, 14 grams of sodium stannate (3H₂O) and 400 mls. of concentrated hydrochloric acid. The previously prepared palladium-stannous chloride mixture is poured into this second solution with stirring to effect complete admixture. This final solution is a concentrated solution containing about 58% by weight concentrated (37%) hydrochloric acid, 32% by weight water, the balance being the palladium and tin salts, and is ready for immediate use upon suitable dilution as hereinafter described. The activating properties of this concentrate can be made still more aggressive by heating it at 120° to 150° F. for about three hours. The solution is highly acid, having a pH substantially below 1.0. It is very stable so that it may be stored for long periods without deterioration.

Chemical plating process

The complete plating process comprises first etching the surface of the plastic substrate with a suitable chemical etchant to prepare its surface for the reception of the activating metal. Various proprietary etchant solutions are available for this purpose but one that is preferred consists of approximately 14% by weight chromic acid, 40% by weight sulfuric acid (66° Bé.), the balance being water. This solution is used at approximately 145° F. and the substrate is immersed in or otherwise contacted with it for a period of 2 to 3 minutes.

The etched substrate is then thoroughly rinsed in water, several times if necessary, and is immediately transferred to an activating solution prepared as in Example I. If the substrate is a printed circuitboard in which through-holes are to be plated, the activator solution of Example I is diluted 1:1 with water and with sufficient additional hydrochloric acid to make up about 20% to 30% of the final volume. For ordinary plating-on-plastics for decorative or protective surface finishing of ABS and similar substrates, the activating solution comprises 15% by volume of the solution of Example I, 10% to 20% by volume of concentrated hydrochloric acid, and the balance water. In either event, the substrate is immersed in or contacted with the activating solution for a minimum of about one minute at ambient room temperature.

The activated substrate is again thoroughly rinsed and preferably subjected to a leaching or accelerating step comprising immersing it in an aqueous solution of fluoroboric acid (48%) at a concentration of about 1 pound per gallon.

Again the substrate is thoroughly rinsed, whereupon it is ready for chemical plating.

Any of a number of conventional copper and nickel electroless plating compositions can be used in this step. In the case of a nickel plate, a suitable plating solution is described in U.S. Pat. No. 2,532,283 Example III, Table II. Similarly, a high suitable copper plating solution is disclosed in U.S. Pat. No. 3,095,309, Example 2. This is followed by electroplating in conventional manner with copper, nickel or any other desired metal.

As has been mentioned, the order or sequence or addition of components in the preparation of the activator sol is relatively critical, as are the concentrations and the elapsed times in certain steps in order that the product be effective as an activator for chemical plating. The foregoing is particularly true in respect of limiting the addition of the initial amount of stannous chloride, where this is used both as reducing agent and protective colloid former, to that amount needed for reducing the palladium. This is illustrated by the following example.

EXAMPLE II

An activator solution is prepared using the same components and proportions as given in Example I above. But instead of adding these components in the manner indicated, the palladium chloride is dissolved immediately in the total amounts of water and hydrochloric acid previously specified. The sodium stannate is then added, followed by addition of the total amount (100 grams) of stannous chloride previously specified.

The resulting solution is then diluted with equal parts of water and used in a standard chemical copper or nickel plating cycle as above described. It is found that in this case the system either fails entirely to produce any chemical deposit of the plating metal, or else the deposit is spotty and so incomplete as to be useless for commercial plating purposes.

Reversing the order of addition of components, i.e., dissolving the total amount of stannous chloride in the hydrochloric acid and then adding the palladium chloride likewise fails to effect activation of a plastic substrate, and no plating, at least none that affords complete coverage and adequate bond or peel strength suitable for commercial requirements is obtained.

In both cases it is noted that the color of the solutions obtained in Example II is different from that obtained by following the procedure outlined in Example I. The difference is further evidenced by testing the solutions for a Tyndall effect. Whereas an activating sol prepared in accordance with the invention exhibits a very definite Tyndall effect, no such effect is noted in the freshly prepared solutions of Example II. However it does appear that if the latter solutions are allowed to age for varying periods, ranging from as little as a few days up to several weeks or more a Tyndall effect will be noticed; and when this Tyndall effect does appear, the solutions are then effective for activation of a substrate. However the length of aging period required for the solution, following its preparation in the manner of Example II, is not readily or accurately determinable. No such problem of aging exists for sols of the invention, since they are operative immediately upon completion of their preparation.

It has also been found that the temperature under which the activator solution is prepared is of importance. If, instead of carrying out the preparation steps at ambient room temperature as described above, the solutions of the several preparatory steps are heated to around 100° F., the resulting sols are more aggressive in their activating properties, tending to cause faster and heavier plating of metal on the substrate in the electroless plating step. This increased aggressiveness is sometimes of advantage, as for example in the plating of printed circuitboard through-holes. It is apparent that the nature of the particle formation is affected by the temperature, as the Tyndall effect changes with the change in operating conditions. This is shown by comparison of various temperature levels maintained in preparing the sols versus Tyndall effect (as measured in terms of percent transmittance) and degree of activation produced by those solutions. The effect on percent transmittance is shown in the following table:

TABLE I

Sample No.:	Temp. of prep., ° F.	Tyndall effect, percent transmittance
1.....	100	34
2.....	110	30
3.....	120	26

NOTE.—Solutions tested for percent transmittance were 2 volume percent activator and 98 volume percent deionized water.

Another variable in the preparation procedure which affects the nature of the resulting sol is the length of time during which the addition of the initial increment of stannous chloride is allowed to react with the palladium chloride before the balance of the stannous chloride is added to the solution. The time of reaction at this step materially affects the particle formation and aggressiveness of the resulting sol. In fact, there is both a minimum and a maximum reaction time which is effective, as illustrated by a comparison of results on substrates activated in the invention sols having the different reaction periods tabulated in Table 2.

Table 2

Mixing time before balance of stannous chloride added	Activation of plastic
6 min.	None.
8 min.	Marginal.
10 min.	Excellent.
12 min.	Do.
14 min.	Excellent (but solution unstable).

The activator solution described in Example I represents a preferred or optimum selection and concentration of components and conditions of preparation, and some variation from such optimum values is permissible without loss of all benefits of the invention. In general, the

concentration of the palladium chloride can be varied to provide the equivalent of from about 0.05 to 5.0 grams of palladium per liter of hydrosol. The amount of reducer must be varied accordingly to provide the equivalent, depending on the amount of palladium actually used, and in the case of stannous chloride would be from 0.10 to 10.0 grams per liter of hydrosol for the amounts of palladium mentioned above. The excess stannous salts used as protective colloid formers should also be varied proportionally. In the case of the sodium stannate, an amount should be added to provide the equivalent of from about 0.35 to 35.0 grams per liter of hydrosol. The same is true for the excess stannous chloride which would vary from 2.40 to 240 grams per liter of hydrosol. Stannous salts other than the chloride are operative as reducing agents and colloid formers but generally are not as compatible in the system.

Without wishing to be limited to any theory or explanation for the improvement resulting from preparing and using the activator hydrosols of the present invention, it is postulated that such improvement is due in large measure to what appears to be a high degree of uniformity in particle size, size distribution and shape in the acid palladium-stannous chloride sols here disclosed. Examination of such sols by the use of the electron microscope gives evidence of the correctness of the foregoing postulation, as in such examination it would appear that it is made up of a majority of particles of substantially spherical shape and small uniform size in an aqueous medium. This is evidenced in freshly prepared sols as well as those that have stood for long periods of time. In contrast, where the conditions of preparation of the activator solutions follow those given in Example II above, no such characteristic particle formation is apparent in freshly prepared solutions or even those which have stood for a matter of hours. In the latter type of solutions it appears that some form of ion complex rather than a true sol is present.

What is claimed is:

1. The method of preparing acid tin-palladium hydrosols suitable for use in activating the surface of non-conductive substrates for the electroless deposition of a conductive metal thereon, which comprises the steps of:

- first dissolving a palladium salt in hydrochloric acid,
- adding to the solution of step (a) an amount of a stannous salt just enough to effect reduction from Pd²⁺ to Pd⁰, and agitating the resulting solution to dissolve the stannous salt therein completely and to effect the reduction;
- separately dissolving in hydrochloric acid additional stannous salt sufficient to form a protective colloid for the reduced palladium and
- admixing the solution prepared in step (b) with that prepared in step (c) while effecting thorough agitation.

2. The method defined in claim 1, wherein the palladium salt in step (a) is palladium chloride in amount to provide the equivalent of from about 0.05 to 5.0 grams of palladium per liter of hydrosol; the stannous salt in step (b) is stannous chloride; and the stannous salt in step (c) is an admixture of sodium stannate and stannous chloride to provide the equivalent per liter of hydrosol of from about 0.35 to 35.0 grams of sodium stannate and from about 2.40 to 240 grams of stannous chloride.

3. The method as defined in claim 2, wherein the preparation of the hydrosol is carried out at room temperature.

4. The method as defined in claim 2, wherein the preparation of the hydrosol is carried out at solution temperatures of from 100° to 120° F.

5. The method as defined in claim 2, wherein the amount of palladium chloride in step (a) is about 2.0 grams, the amount of stannous chloride in step (b) is about 4.0 grams, the amount of sodium stannate and

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stannous chloride in step (c) are, respectively, about 14 and 96 grams.

6. The method as defined in claim 5, wherein the agitation in step (b) is continued for 12 minutes, followed immediately thereafter by step (d).

7. The method defined in claim 1, wherein the palladium salt in step (a) is palladium chloride and the stannous salt in step (b) is stannous chloride.

8. The method defined in claim 7, wherein the stannous salt in step (c) is also stannous chloride.

9. An acid stannous chloride-palladium hydrosol wherein the metal particles are of substantially uniform spheri-

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cal shape and size, said hydrosol having been made according to the method of claim 1.

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RICHARD D. LOVERING, Primary Examiner

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