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CATALYST FOR ELECTROLESS PLATING

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U.S. Cl. 252—430 2 Claims

ABSTRACT OF THE DISCLOSURE

A lyophilic material is prepared by hydrolysing egg albumen with a solution of lithium hydroxide, precipitating out lithium by treatment with carbon dioxide and filtering, precipitating out the remainder of the lithium by treatment with phosphoric acid and filtering; adding acetic acid to the resulting liquor and filtering off the precipitate which is the lyophilic material. For use as a colloid the lyophilic material is dissolved in lithium hydroxide to form an unusually robust colloid. A preferred use for this colloid is as a protective colloid to protect colloidal metal particles (e.g. palladium) in a catalyst for use in electroless plating.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The invention pertains to lyophilic materials and methods of preparing them for use in electroless plating processes and more particularly concerns such materials and methods whereby albumen is treated to form a lyophilic material for protection of colloidal metallic particles such as palladium in a catalyst for use in electroless plating.

(2) Description of the prior art

This invention relates to electroless plating, i.e. the deposition of metal out of a solution of one of its compounds on to a substance immersed therein without transfer of electric current from an external source. In order that the deposition takes place preferentially on the substrate to be plated this is treated with a sensitizer followed by treatment in an activating catalyst before immersion in the plating solution. In this catalyst treatment colloidal particles of a metal catalytic to the chemical deposition process are absorbed by the surface of the substrate, in which position they act as seeds promoting nucleation of metal for further growth out of the plating bath.

The method of metal coating by electroless plating requires that the thickness of the coating be comparable with that which is encountered in similar electroplated deposits, and for that reason the preferred coating metals are those which are autocatalytic, that is to say, metals which deposit and catalyse further metallic reduction from the plating solution. Many such metals are known, notably gold, silver, nickel, cobalt, copper, and metals of the platinum family of metals.

In one prior art electroless plating process the substrate is first thoroughly cleaned and then treated for a few moments in a sensitizing bath for example consisting of an aqueous solution of stannous chloride, hydrochloric acid and a wetting agent, for example cetyl pyridinium chloride, or an agent known as Teepol. The substrate is then rinsed in water and transferred to a bath containing the catalyst which may be a metal chloride taken from the group comprising gold, silver and the elements of the platinum family, but preferably palladium chloride dissolved in water acidulated with hydrochloric acid. After allowing the substrate to remain in the catalyst solution for 2 to 5 minutes, it is rinsed and finally placed in a plating bath containing, for example, Rochelle salt, sodium hydroxide, copper sulphate, and formaldehyde, out of which metallic copper can be deposited on the substrate.

In the sensitizing bath stannous ions are absorbed at random on the substrate. These ions act as reducing agents towards catalyst solutions e.g. solutions of palladium chloride becoming the parents of catalytic nuclei of palladium ions. In has been found that in repeated use of the catalyst solution there first occurs a gradual improvement in its activity, but later activity declines rapidly and terminates quite suddenly. It is theorized that this is because the rinse between the sensitizing bath and catalyst solution bath does not entirely eliminate carry-over of the stannous chloride and detergent into the catalyst bath. Although the mass transferred is small in any single operation there is a cumulative effect in repeated operations. The carry-over of stannous chloride into the palladium chloride solution produces palladium and stannic acid, both as lyophobic colloids, and the latter acts as a protective colloid toward the first. Because of the high catalytic activity of those colloidal particles the initial improvement referred to above occurs. This effect only continues so long as the concentration of hydrochloric acid is sufficient to inhibit coagulation of the colloidal particles so that they can no longer remain in suspension. With the increasing concentration of stannic acid particles in the catalyst solution, the competition between the formation of new colloidal nuclei and the growth of nuclei already present goes in favour of the latter, and a point is reached where there are insufficient acid ions in the sol and the particles coagulate, so diminishing the activity of the catalyst solution.

It has also been proposed in the prior art to take advantage of the increased catalytic activity due to colloid formation by deliberately forming a colloid of palladium particles protected by another colloid. Such a catalyst is described in U.S. patent specification 2,430,581, which uses colloidal palladium with a protective colloid of polyvinyl alcohol, methyl cellulose, or glue.

SUMMARY OF THE INVENTION

This invention is concerned with an improved catalyst mixture of the kind in which advantage is taken of the increased catalytic activity due to colloid formation.

The invention provides a catalyst for use in electroless plating which comprises a colloidal suspension of metal particles catalytic to the plating process and a lyophilic colloid to act as a protection for said metal particles, said lyophilic colloid being formed from a lyophilic material obtained by hydrolysing egg albumen with a solution of lithium hydroxide and treating the product with acetic acid. The pH value of the catalyst is preferably between 12 and 12.4.

According to another aspect the invention provides means for preparing the catalyst set out above, comprising two separate concentrated solutions for dilution and mixing to form the catalyst, said concentrates comprising solution A which is a solution of palladium chloride and solution B which is a solution of said lyophilic material, and a reducing agent.

The invention also provides a method of preparing a lyophilic material, comprising the steps of hydrolysing egg albumen with a solution of lithium hydroxide, removing the lithium by precipitation with carbon dioxide and phosphoric acid, or with phosphoric acid, and thereafter precipitating the required lyophilic material with acetic acid. The invention also extends to the lyophilic material formed by this method.

A lyophilic material was prepared from egg albumen by C. Paal many years ago, and was given the name protalbic acid. It is not certain whether or not the lyophilic material prepared according to the invention is the same as that of Paal, and there is some evidence to show that the hydrolysis method of the invention, which is different from that of Paal, may have influenced the constitution of the material. For convenience we have hereinafter referred to the material as protalbic acid, but it will be understood that by this it is intended to mean the product of the method of the invention as set forth herein.

DESCRIPTION OF THE PREFERRED EMBODIMENT

The invention is of particular use in plating metals, e.g. copper, onto substrates of semi-conductors or dielectric materials for example for printed circuit boards. These last are usually composed of fibres of mineral or organic matter bonded with a synthetic resin, for example, glass fibres bonded with epoxide resin. Such boards may be clad on one or both sides with a thin laminate of copper which is secured to the dielectric substrate with adhesive. By a known photographic process and masking technique involving the use of etchant resist, a network of conductors is formed from the copper laminate, the unwanted areas being dissolved away. Connections may then be required between the two sides of the board and this is done by drilling holes between the parts to be connected and electroless plating the inside surface of the holes. This part of the technique is known as "through-hole plating" and has lead in the past to difficulties due to poor adhesion of the plated metal to the copper laminate.

A specific example of the preparation of a catalyst according to the invention is now described.

700 ml. of demineralised water was introduced into a 5 litre borosilicate glass beaker, and 38.5 g. of dried egg albumen powder was added gradually, with constant stirring until all the powder was dissolved. The mixture is gently warmed to assist solution. A solution of 90 g. lithium hydroxide mono-hydrate in 1220 ml. demineralised water was added to the albumen solution with constant stirring. The mixture was then heated, with occasional stirring until it began to boil. It was kept boiling vigorously for about 1 hour to complete hydrolysis, during which time its volume was reduced by about ⅔. The resulting liquor was allowed to cool and carbon dioxide was then passed through it for 6–7 minutes, the flow of gas being adjusted to prevent too much foaming. This precipitated lithium carbonate. This mixture was then filtered and the precipitate conserved for reconversion to lithium hydroxide for re-use. A second passage of gas was made to ensure full combination. The solubility of lithium carbonate (Li_2CO_3) at 0° C. is 1.54 g./100 ml. H_2O and at 100° C. is 0.72 g. It is however more soluble in carbonated water. The carbon dioxide was therefore expelled from the solution by boiling and the solution was filtered as hot as possible. This produced a second crop of lithium carbonate which was added to the first. A total of 70 g. of dry lithium carbonate was recovered. This represented an approximate recovery efficiency of 89%. The remaining filtrate was mainly a solution of the lithium salts of protalbic and lysalbic acids, volume 780 ml.; pH value 9.8.

The remaining lithium in solution was then precipitated as insoluble phosphate (Li_3PO_4) by slowly adding, with constant stirrings, 25% orthophosphoric acid until the pH dropped to 6.9. The solution was boiled and the protalbic acids in the form of their lithium salts. This solution was cooled and 25% acetic acid added until pH 4.3 was reached. This precipitated the protalbic acid which was then filtered out.

The filtrate was washed 5 times with water and the resulting wet protalbic acid was gently dried.

When required for use the protalbic acid was dissolved in 10% lithium hydroxide solution and water and a few drops of hydrazine hydrate added. Then with vigorous mechanical agitation a solution of palladium chloride acidulated with hydrochloric acid was slowly added. The mixture rapidly went black forming lyophobic palladium particles protected by the lyophilic lithium salt of protalbic acid. This mixture remained stable. The amount of palladium chloride added was such that the final colloidal mixture contained 1 gm. per litre of palladium chloride. The pH value of the mixture was between 12 and 12.4 as taught in original claim 3.

Other salts of protalbic acid may be suitable for use in forming the protective colloid e.g. the sodium or potassium salts.

It will be noted that virtually all the constituents of the catalyst mixture are in true solution except for the palladium particles and the protective colloid. Therefore the catalyst mixture is particularly efficient since when it is applied to a substrate to be plated substantially all the available positions on the substrate are occupied by the catalytically active palladium. Where a solution contains other particles which are catalytically inert, these particles must be expected to occupy their proportion of the available positions and thereby reduce the efficiency of the catalyst and the strength of the bond of the plated metal onto the substrate. The catalyst is also alkaline, which avoids the difficulty of transporting acid materials.

The lyophilic colloid is not only an effective protection for the palladium and therefore stabilises the solution but it also has pronounced surface active properties which enhance wetting the surface of the substrate.

In the preparation of the lyophilic colloid the precipitation procedure described removes substantially all the electrolytic material which would contaminate the catalyst solution and increase the tendency of the palladium particles to coagulate. Just sufficient residual salt is left to enable an electrical double layer to be established on the lyophobic colloidal palladium particles.

In variations of the specific example cited above, the concentration of egg albumen may be increased.

An electroless plating process using the above catalyst mixture comprises the steps of first cleaning a copper substrate and then immersing the cleaned substrate in a sensitizing bath. This bath may comprise stannous chloride in solution.

The substrate is then removed and rinsed and transferred to the catalyst mixture described above. The substrate is again dipped in water and placed in a chemical copper plating bath. Plating activity is markedly rapid and results in a copper cladding firmly adherent to the copper substrate. Using the specific catalyst described above a layer of thickness 0.00015 inch of copper was produced in about 25 minutes.

While the above examples are concerned with the preparation of a palladium catalyst, similar methods using the same protective colloid can be employed to produce platinum and gold for use as catalysts. Methods of preparing hydrosols of these metals are to be found in the prior art, particularly those published by C. Paal as described in "Text Book of Inorganic Chemistry" by J. Newton Friend volume IX, part 1, page 270.

A preferred method of producing protalbic acid on a large scale comprises the steps of reconstituting 500 g. of dried egg albumen (flake) in 5 litres of water in a stainless steel bucket. 250 g. of lithium hydroxide ($LiOHH_2O$) dissolved in 2500 ml. of distilled water is added to the albumen with mechanical agitation. The resulting liquor is then heated to boiling and maintained at boiling point for 30–40 minutes to hydrolyse the albumen. Any insoluble matter in suspension is then filtered off. It is preferred to allow the precipitate to settle before filtration and to decant off as much of the liquor as possible as the insoluble matter forms an almost impervious coating over the filter paper. A Buchner funnel using a No. 54 paper is used.

The filtrate is reboiled for about 1 hour until there is no further smell of ammonia in the vapour given off, and is then cooled to 40° C. or below. Carbon dioxide is then vigorously passed for 5–12 minutes. The carbonate precipitate is allowed to settle and then filtered. The precipitate is dried at 110° C. for 12 hours yielding about 133 gms. and leaving a filtrate of volume about 4600 ml.

The filtrate is boiled with constant vigorous mechanical agitation to expel the carbon dioxide and to convert any bicarbonate to the more insoluble carbonate. It is then filtered as hot as possible and the precipitate added to the first carbonate precipitate. The volume of the filtrate is now about 3700 ml. at pH 10.75. Weight of dry carbonates filtered out is 118 gm.

Phosphoric acid H_3PO_4 25% is added to the filtrate to convert all remaining carbonate to phosphate. This is done under mechanical agitation, the volume of acid added being 120 ml. giving a pH of 7. The precipitated phosphate is allowed to settle and is then filtered out.

25% acetic acid is then added to the filtrate to precipitate protalbic acid. The volume of acid added in this example was 240 ml. bringing the pH to 4.3.

The precipitated protalbic acid is filtered off, washed and dried. In one example a yield of 22.5 g. dry protalbic acid was achieved. The dried protalbic acid was then available for use in a catalyst composition as described above.

The markedly rapid plating referred to above is attributed to the increased efficiency of the catalyst. It may be preferred to reduce the rapidity of plating by reducing the concentration of palladium in the catalyst, so using the said increased efficiency to reduce the palladium requirement rather than the speed of plating.

In an example of a catalyst with a reduced palladium content, the catalyst is prepared as two solutions designated solution A and solution B each of which has a very long shelf life. When required for use the solutions are mixed as described hereinafter to form the colloidal catalyst. Lyophobic colloidal suspensions are by their nature somewhat delicate and the particles are easily caused to coagulate and come out of suspension, and it is for this reason that the lyophobic palladium colloid preferably is not formed during storage. However, when the colloidal catalyst is mixed ready for use it is found to be exceptionally robust, for a colloid.

Solution A comprises a concentrated solution of palladium chloride in water acidulated with hydrochloric acid, the solution containing 6 grams of palladium chloride per litre. This solution is only slightly acid.

Solution B comprises protalbic acid dissolved in a solution of 10% lithium hydroxide to form the lithium salt of protalbic acid. The solution also contains about 1.2 ml. hydrazine hydrate per litre of solution. The preferred concentration of protalbic acid is 5 grams per litre. This solution is very alkaline.

To prepare the catalyst equal volumes of solutions A and B are taken and each is diluted separately by ten times the volume of water. Solution A is then added to solution B slowly and with vigorous agitation, whereupon the palladium chloride is reduced to colloidal palladium forming a black colloidal suspension which is stable for long periods. In the final catalyst the concentration of palladium is equivalent to that obtained from a 0.3 gram per litre solution of palladium chloride. The catalyst has a pH value of between 12 and 12.4.

At this concentration the catalyst still causes exceptionally rapid plating but is cheaper due to the smaller proportion of palladium.

I claim:

1. A catalyst for use in an electroless plating process which consists essentially of:
- a suspension of metal particles catalytic to said plating process, and
- a lyophilic material forming a protective layer on said particles, said lyophilic material being formed by:
  - hydrolyzing egg allbumen with an aqueous solution of lithium hydroxide,
  - removing substantial portions of the said lithium by precipitation with carbon dioxide, and then with phosphoric acid, and
  - precipitating the said lyophilic material with acetic acid,
- said lyophilic material and said suspension being suspended in an aqueous solution of lithium hydroxide having a pH value lying between 12 and 12.4.

2. The method of preparing a catalyst for use in an electroless plating process consisting essentially of:
- hydrolyzing egg albumen with an aqueous solution of lithium hydroxide,
- removing substantial portions of said lithium by precipition with carbon dioxide, and then with phosphoric acid,
- precipitating lyophilic material from said aqueous solution with acetic acid,
- placing said lyophilic material in a ten percent by weight aqueous solution of lithium hydroxide,
- adding a reducing agent to said lithium hydroxide solution, and
- adding an acid solution of palladium chloride in water to said lithium hydroxide solution.

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U.S. Cl. X.R.

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