

Method for metallising dielectric substrates using aqueous colloidal solutions

The present invention relates to a method for metallising dielectric substrates, the use of aqueous colloidal solutions in such methods, aqueous colloidal solutions and aqueous developer solutions and the products obtainable by such method.

A feature common to all metallisation techniques is the deposition of a very thin layer of metal on a non-conducting plastic surface without using an outside source of current. This thin layer, while satisfactory for many applications, is extremely sensitive to abrasion and corrosion. Any additional requirements over and above purely decorative effects, for example in respect of hardness, abrasion resistance, corrosion resistance and electrical conductivity, necessitate electrolytic thickening. The thin layers of metal are usually obtained by the method described in Document I.

Document I discloses a method for the manufacture of printed circuits in which the wettable plastic surface is first "activated" or "nucleated" with silver or palladium prior to metallisation in a chemical metallisation bath.

Document II discloses aqueous colloidal solutions of hydrated oxides of copper which are highly suitable for use as fungicides.

It has now been found that certain aqueous colloidal solutions can be used in a method which improves the adhesion of the metal layer to the substrate surface and also enables economic advantages to be achieved by reduction of treatment times and in some cases products of more uniform quality.

According to the present invention there is provided a method for metallising dielectric substrates comprising the steps:-

- (I) (a) treating a wettable surface with a colloidal aqueous solution of a hydrated oxide or a hydrated oxide mixture of copper, nickel and/or cobalt;
- (b) rinsing with water to remove excess colloid;
- (c) treating the surface with an aqueous developer solution;
- (d) further rinsing with water; and
- (II) carrying out electroless metallisation of the surface; and
- (III) optionally electrolytic thickening of the resulting metal layer.

Process steps (I) and (II) are usually carried out by immersion.

Our process is suitable not only for manufacturing printed circuits but also quite generally for applying metallic coatings to various substrates such as glass or plastic surfaces.

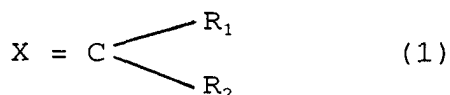
The colloidal solution of hydrated oxide or of hydrated oxide mixture can be made by the process described in Document II. The colloidal, hydrated particles of oxide are so small that they behave in many respects like molecules, but they are large enough to exhibit the properties of discrete particles with interfaces. This colloidal dispersion state and the interfaces modified by water molecules are probably the main reason for the improvements obtained.

It is generally desirable to increase the stability of the colloidal solution. If the solution is stored or used over a fairly long period, however, it becomes essential. To improve the stability, stabilisers are added to the solution, which are absorbed onto the colloidal particles and produce a change in their charge characteristics. This suppresses the tendency for the particles to coagulate.

Thus in a further aspect of the invention the use of certain known and novel aqueous colloidal solutions is claimed (as defined in claim 1 or 2).

The substances normally used to stabilise colloidal systems, e.g. gelatine, gum arabic and cellulose derivatives, such as carboxymethyl cellulose and hydroxypropyl cellulose, can be used as stabilisers for the colloidal solutions.

Known compounds of the formula



in which X is oxygen or sulphur and R₁ and R₂ are an amino group or an alkyl group with 1 to 6 carbon atoms, have been found to have a quite specific stabilising effect in colloidal solutions also containing a hydrated oxide of antimony.

The stabilising effect of these compounds is in fact so pronounced that the colloidal solutions can, in addition, contain a reducing agent, thus enabling the entire metallisation process to be shortened, because much less time is needed for carrying out treatment with the colloidal solution and with the developer solution in the activation process. An aqueous developer solution containing a reducing agent causes the metal ions of the colloid absorbed on the surface of the substrate to be reduced to a lower oxidation state, enabling them to become active in the electroless deposition of metal.

Thus according to a further aspect of the invention an aqueous developer containing a reducing agent is claimed.

It has been found that stabilisation can be achieved better, and at a lower concentration of stabilisers, if the colloidal solution also contains a hydrated oxide of antimony, preferably amounting to 15 - 50 mol% of the total quantity of hydrated metal oxides. The production of such colloidal solutions is likewise carried out by the process described in Document II.

In the colloidal solution and in the developer solution the usual reducing agents, such as alkali metal borohydrides, alkaline-earth metal borohydrides and diethylamine borane may be employed.

The concentration of reducing agent in the developer solution is preferably 1.2 - 2.5 g/l. At lower concentrations the developing time is lengthened to a technically unacceptable degree. Higher concentrations provide no advantages and would therefore make the process needlessly more expensive.

The concentration of reducing agent in the colloidal solution depends on the stabilising effect of the compounds of formula (1). These compounds, which, by the way, are used preferably in a concentration of 0.5 - 2.5 g/l, show in fact different stabilising activities.

Those compounds of formula (1) in which $X = S$ permit a maximum reducing-agent concentration of 2.6 g/l without significantly impairing the colloidal solution's stability. At higher concentrations, however, the colloidal solution grows so unstable that it quickly ages and becomes unusable. What matters is that if the concentration of reducing agent is at least 1.9 g/l a separate developer solution can be dispensed with.

On the other hand, the concentration of reducing agents in the presence of formula (1) compounds in which $X = 0$ may not exceed 1.5 g/l, in view of these compounds' lesser stabilising effect.

A hydrated oxide of antimony must always be present in colloidal solutions containing even a very low concentration of reducing agents since the solutions would otherwise be irreversibly destabilised. The addition of a conventional stabiliser such as gelatine has practically no influence at all on the destabilising effect of the reducing agent.

Thus in a further aspect of the invention novel aqueous colloidal solutions containing such oxides and a stabiliser and/or a reducing agent are claimed.

In a yet further aspect of the invention there is provided a product obtainable by the method as disclosed herein.

Some examples of the preparation of colloidal solutions are given below. The colloidal solutions always contain enough stabiliser to give them almost unlimited stability at room temperature and to ensure that they are sufficiently stable under working conditions to function problem free as an activating component. The stabiliser needs to be added because the colloidal system is irreversible, in other words the hydrated oxides cannot be returned to the colloidal state after precipitation or drying out.

Example A:

An aqueous colloidal solution was prepared by adding 0.5 molar ammonium hydroxide to 200 ml of 0.25 molar copper acetate whilst mixing thoroughly at 63°C, until a pH of 10.4 was reached. The solution was then allowed to react for five and a half hours at 65°C with stirring, the pH being kept at 10.3 - 11.0 through the addition of ammonium hydroxide. The resulting colloidal solution was then stabilised with 7 g/l of hydroxypropyl cellulose.

Example B:

An aqueous colloidal solution was prepared in the same way as in Example A, except that the copper acetate solution also contained 0.1 mol/l of SbCl_3 . Only 3.7 g/l of hydroxypropyl cellulose was needed to achieve the same degree of stabilisation.

Example C:

To prepare a colloidal solution, an aqueous solution containing:

CuCl_2	7.3 g/l
SbCl_3	7.3 g/l
$(\text{NH}_2)_2\text{CO}$	2.0 g/l
NaBH_4	1.4 g/l

was hydrolysed as in Example A, with NaOH as the base.

Example D:

A colloidal solution was prepared as in Example A, the copper-salt solution having the following composition:

CuCl_2	7.3 g/l
SbCl_3	7.3 g/l
CH_3CSNH_2	1.96 g/l
NaBH_4	2.4 g/l

Example E:

A colloidal solution was prepared as in Example D, using the compound $(\text{NH}_2)_2\text{CS}$ instead of CH_3CSNH_2 , in an amount of 2.5 g/l.

The colloidal solutions in Examples A to E were used to activate an ABS substrate (copolymer of acrylonitrile-butadiene-styrene) made wettable by etching in a solution containing 400 g/l of chromium oxide and 350 g/l of concentrated sulphuric acid. The substrate was first immersed in one of the colloidal solutions, then rinsed with desalinated water and, if desired, subsequently immersed in a developer solution containing 1.9 g/l of KBH_4 . The immersion times are given in the table below. The activated substrate was then rinsed again and immersed for 10 minutes in an electroless aqueous

copper bath of known composition maintained at a temperature of 40°C. The copper bath contained the following components:

CuSO ₄ . 5H ₂ O	15 g/l
EDTA (40%)	68 g/l
NaOH	9 g/l
Tergitol TMN	20 g/l
HCOH (37%)	25 g/l

A layer of copper approximately 0.3 µm thick was thus deposited on the plastic and this thin layer of metal was then thickened electrolytically in the usual way. The same conditions were maintained for each test.

The stripping force was measured on respective flat surfaces (according to DIN 53 494) to determine the adhesion of the thickened copper layers. These values were then compared with the stripping force needed for a copper layer whose production differed only in that the activation was carried out according to Document I using a tin (II) chloride solution and an ammoniacal silver-nitrate solution. It was found that, with the colloidal solutions A to E according to the invention, adhesion was approximately 2.7 times better in all cases. Differences in the composition between solutions A to E thus had no effect on the degree of adhesion and on the quality of the metal layers.

Similar effects were found in other tests in which the colloidal solution contained a hydrated oxide of nickel or cobalt. However, adhesion was around 15% less than with colloidal solutions containing hydrated copper oxide.

The treatment times needed for activation with solutions A to E are given in the following table:

Table

Colloidal solution	Treatment time with colloidal solution (min.)	Treatment time with developer solution (min.)
A	13	15
B	13	11
C	7	5
D	3	-
E	3	-

It should be noted in connection with these test results that short treatment times are extremely important for economical metallisation on an industrial scale. Likewise, elimination of the developing bath is highly advantageous as it not only avoids two

stages in the activation - intermediate rinsing and developing - but also ensures a more uniform quality.

Claims

Claim 1.

Use of an aqueous colloidal solution of a hydrated oxide or a hydrated oxide mixture of copper, nickel and/or cobalt for activation of a substrate's surface in a method of metallising dielectric substrates by electroless metallisation.

Claim 2.

Use of an aqueous colloidal solution according to claim 1 which further comprises a stabilizer selected from gelatine, gum arabic or cellulose derivatives.

Claim 3.

An aqueous colloidal solution of a hydrated oxide of nickel or cobalt, or a hydrated oxide mixture of copper, nickel and/or cobalt.

Claim 4.

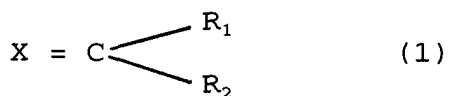
An aqueous colloidal solution according to claim 1 or 3 which further comprises a suitable stabilizer provided that when the hydrated oxide is of copper then the stabilizer is not gelatine or gum arabic.

Claim 5.

An aqueous colloidal solution of a hydrated oxide or a hydrated oxide mixture of copper, nickel and/or cobalt, comprising said oxide, a suitable stabilizer and a hydrated oxide of antimony.

Claim 6.

An aqueous colloidal solution according to claim 5 wherein the stabilizer is a compound of formula (1)



in which X is oxygen or sulphur and R_1 and R_2 are independently either an amino group or an alkyl group with 1 to 6 carbon atoms.

Claim 7.

An aqueous colloidal solution according to claim 6 wherein the concentration of the compound of formula I is from 0.5 to 2.5 g/l.

Claim 8.

An aqueous colloidal solution according to claim 6 or claim 7 which further comprises a reducing agent.

Claim 9.

An aqueous colloidal solution according to claim 8 wherein in the compound of formula (1), X is sulphur and the concentration of reducing agent is at least 1.9 g/l and not more than 2.6 g/l.

Claim 10.

An aqueous colloidal solution according to claim 8 wherein in the compound of formula (1), X is oxygen and the concentration of reducing agent is not more than 1.5 g/l.

Claim 11.

An aqueous developer solution further containing a reducing agent in the concentration of from 1.2 to 2.5 g/l.

Claim 12.

Method for metallising dielectric substrates comprising the steps:-

- (I) (a) treating a wettable surface with a colloidal aqueous solution of a hydrated oxide or a hydrated oxide mixture of copper, nickel and/or cobalt;
- (b) rinsing with water to remove excess colloid;
- (c) treating the surface with an aqueous developer solution;
- (d) further rinsing with water; and
- (II) carrying out electroless metallisation of the surface; and
- (III) optionally electrolytic thickening of the resulting metal layer.

Claim 13.

Method for metallising dielectric substrates according to claim 12 wherein the colloidal aqueous solution is as defined in any of claims 1 to 8 and 10.

Claim 14.

Method for metallising dielectric substrates comprising the steps.-

- (I) (a) treating a wettable surface with a colloidal aqueous solution as defined in claim 9;
- (b) rinsing with water to remove excess colloid; and
- (II) carrying out electroless metallisation of the surface; and
- (III) optionally electrolytic thickening of the resulting magnetic layer.

Claim 15.

Method for metallising dielectric substrates according to claims 12 and 13 wherein the aqueous developer solution is as defined in claim 11.

Claim 16.

A product obtainable by the method of claims 12 to 16.

Note to Examiners

Use, method and product claims for Spain.

No change for Greece.

In retrospect I would put the reducing agent in the developer in all relevant claims since I now suspect it does not work without it.

Also I would want to check with the inventor as to whether the limits for compound I $X = 5$ and $X = 0$ are really that rigid, since presumably stability is not an issue if the next step is immediate. If they are rigid I would write the limitations into claim 6.

There are four claim categories which I would consider unified.