

Candidate's examination paper (Examination paper B/1990 Chem

To: EPO, Munich

Dear Sir,

Re: EPA -

I refer to your communication pursuant to Art. 96(2) dated and enclose herewith in triplicate replacement claims for this case, together with three copies of pages 1 to x of the description. The claims have been amended in order to overcome the Examiners objections based on Documents III and IV and the description has been revised for consistency therewith. A copy of the amended pages of the description amended in manuscript is also enclosed herewith for the Examiner's convenience.

Documents III and IV are acknowledged by the applicant to represent prior art relevant to the present invention, although Document IV may only be considered to be prior art for novelty purposes in accordance with Art. 54(3) EPC and cannot be used to attack the inventive step involved in the present application. In order to set the invention out more clearly in relation to these fresh items of prior art, an acknowledgement of their disclosures has been inserted into the introduction on pages 1 to 2 of the present application. The applicants have also taken this opportunity to redefine the technical problem which has been overcome by the invention in the light of Document III. The mere acknowledgement of prior art in this way has been accepted by the Technical Boards of Appeal not to contravene Art. 123(2) EPC and the applicants submit that their acknowledgement does not constitute "added matter" and does not extend the content of the application as filed. Furthermore, the restatement of the problem and its solution has also been permitted by the Boards of Appeal, particularly when fresh prior art which is pertinent to the invention has been discovered.

Document III, as the Examiner has pointed out in Item 1 of his letter, describes the use of aqueous colloidal solutions to activate dielectric substrates. The solutions contain hydrated oxides of copper, iron, nickel or cobalt and thus the subject matter of original claim 1 is anticipated and not patentable in view of Art. 54(1) EPC. Document III also discloses the stabilising effect of hydrated oxides of tin or antimony and particularly stabilisation by these oxides in the presence of a urea compound of formula $RCONH_2$ in which R is an amino group or an alkyl group with 1-10 carbon atoms. Only a single specific urea compound is presented in the Example, that is the compound in which R is an amino group $(NH_2)_2CO$. Nevertheless, a number of Technical Boards of Appeal have held that an enabling disclosure exists where a simple choice of one group from a number of alternatives is required and that such generically disclosed compounds are effectively disclosed per se, even if no specific examples are given. Thus where R is an amino group or an alkyl group of 1-10 carbon atoms is defined, each specific compound where $R=NH_2$, C1-alkyl (methyl) and C10-alkyl are effectively specifically disclosed and $R=C2-9$ alkyl are also disclosed unless a specific and unexpected advantage can be

attributed to this particular range. For this reason the applicant concurs with the Examiner's view that original claims 1 to 4 are anticipated by Document III.

Document III also suggests that "small" quantities of a reducing agent may be included in colloidal solutions containing a urea compound and a hydrated oxide of tin or antimony and thus original claim 5 also lacks novelty.

For the reasons discussed above the applicants have deleted original claims 1 to 5 of the application but have incorporated the prior art features disclosed in Document III into the pre-characterising part of replacement claim 1. The stabiliser of use in the present invention, the compound of formula (1) as originally defined in original claim 1, has been restricted to exclude the compounds of formula (1) in which X is oxygen. This restriction excludes colloidal solutions disclosed in Document III which contain a number of compounds of formula (1) in which X is oxygen, namely those in which R_1 is NH_2 and R_2 is NH_2 or alkyl. Although Document III does not disclose the use of compounds of formula (1) in which X is oxygen and R_1 and R_2 are alkyl, the applicants do not consider that the use of such compounds involves any inventive step over the disclosure in Document III.

Amended claim 1 has been further characterised by the concentration of reducing agent used in the solution, namely 1.9 to 2.6 g/l. Basis for this limitation is provided in the last paragraph of original page 5 of the application as filed. The restriction to this range of reducing agent concentration further distinguishes the invention from the disclosure of Document III which refers only to the use of "small quantity of a reducing agent". The use of relatively high concentrations of reducing agent, possible only with the sulphur-containing compounds of formula (1), is highly advantageous since at concentrations of at least 1.9 g/l a separate developer solution can be dispensed with (original page 5, last paragraph), treatment times are short and a more uniform quality of metallising is attained. These factors are extremely important for economical metallisation on an industrial scale, as already mentioned on page 10 of the application as originally filed. The shortened activation times attained by the invention are illustrated in the Table on original page 10 which compares Examples D and E of the invention with a number of alternative colloidal solutions either disclosed or suggested by the prior art.

The applicant has taken this opportunity to amend the claims of his own volition in accordance with Rule 86(2) and has inserted new claims 2 to 4, which are dependent on new claim 1 and are novel and inventive for the reasons discussed above. The features incorporated into claims 2 and 3 are adequately based on the specific compounds of formula 1 disclosed in Examples D and E, and basis for the concentration range defined in new claim 4 may be found in the third paragraph on original page 5 of the application as filed.

Document IV has also been briefly acknowledged in the introduction of the revised specification. As discussed previously it can only be used to form the basis of a novelty attack against the present

invention. It generically describes a group of stabilising compounds having superior properties when compared to the urea compounds disclosed in Document III. These compounds have the formula:

R_1CSR_2 in which R_1 is C_{1-5} alkyl or C_{6-8} aromatic and R_2 is NH_2 , C_{1-5} alkyl or halogen.

Preferred compounds are suggested to be those which contain a halogen atom and only a single compound in which R_1 is $n-C_3H_7$, and R_2 is Cl is specifically disclosed. A number of Technical Boards of Appeal have held that the generic disclosure of a group of compounds containing two variable substituents, each of which may be selected from a number of different groups, does not specifically disclose each individual compound which can be obtained within the generic formula. The specific compounds in which R_1 and R_2 each independently represent an alkyl group or an amino group are therefore not disclosed in this patent application in the absence of any specific direction to the use of these compounds. For this reason the Examiner is incorrect in his assertion that the disclosure of Document IV is also relevant to the novelty of original claims 4 and 5. No specific disclosure of the use of the compounds claimed is made in Document IV and accordingly the subject matter of new claims 1 to 4 is novel over the disclosure in Document IV.

In item 3 of the Examiner's letter it is stated that the processes claimed in original claims 6, 7 and 8 are known. The applicants concur that the process claimed in original claim 6 is substantially identical to the process described for the preparation of colloidal solutions in both Documents III and IV and thus original claim 6 has been deleted. However, original claim 7 has been amended to correlate with the inventive solution claimed in claims 1 to 4 (which obviates the need for separate treatment with a developer solution) and has been made dependent on these claims. Accordingly, the novelty and inventiveness of the product utilised in the process, supports the patentability of the process claimed. In any event, the process is itself novel and inventive over Document III since the use of a single activating solution (i.e. without separate developer) is new and could not have been predicted from the prior art.

New claim 6 is based on original claim 8 and is patentable for the reasons discussed for claim 5 since it is dependent thereon.

The description has been amended for consistency with the revised claims and the typographical errors occurring on the original page 8, Examples D and E have been corrected in accordance with Rule 88 EPC.

The applicants also submit herewith in triplicate a set of claims for Spain, in view of its reservation under Art. 167 in respect of chemical products. These claims are based on new claims 5 and 6 and simply correspond to process claims in respect of the use of the solutions claimed in original claims 1 to 4.

In agreement with item 4 of the Examiner's letter, original of the application has been deleted since the metallised objects produced according to the invention are not themselves distinguished over the art.

In the event that the above comments are not deemed persuasive the Examiner is requested to telephone the applicant's representative or invite him to an interview to discuss the matter. Alternatively, the applicant hereby requests oral proceedings under Art. 116 EPC.

Colloidal solutions containing hydrated metal oxides and a stabiliser, process for activating dielectric substrates and process for producing metallised dielectric substrates.

The invention relates to in part new aqueous colloidal solutions of hydrated metal oxides and a stabiliser, activation of dielectric substrates with the said colloidal solutions and also coating of the activated substrates by electroless metal deposition, and, where necessary, thickening of the resulting thin metal layer by electrolytic metal deposition.

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.

These thin layers of metal can be obtained by the method described in Document I, whereby the wettable plastic surface (after cleaning, as necessary) is first "activated" or "nucleated" with silver or palladium. For nucleation with silver, for instance, the surface is first immersed in a tin(II)chloride solution and, after intermediate rinsing, then immersed in an ammoniacal silver-nitrate solution. Nucleation with palladium requires the use of an ionogenic palladium salt solution, followed by rinsing and immersion in a solution containing a reducing agent. Nucleation with 0.1 - 1.0 mg/dm² of noble metal is a prerequisite for the specific deposition of metal by chemical means.

The chemical metallisation baths currently used contain the metal (Cu or Ni), in the form of an aqueous complex salt solution, and a chemical reducing agent, e.g. sodium hypophosphite or diethylamino borane for nickel baths, and formaldehyde for copper baths. Each formulation is such that metal deposition only begins upon immersion of the nucleated workpiece and stops upon its removal. Usually a coherent layer of metal approximately 0.3 μm thick is deposited within 10 minutes on the plastic. This thin layer of metal can then be thickened in the usual way by electrolysis.

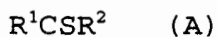
Disadvantages of the known method are that the electrolessly deposited thin metallic layer and the electrolytically thickened layer still adhere unsatisfactorily and that expensive noble metal salts are needed for the activation process.

A new process which utilises non-noble metals has recently been disclosed in Document III.

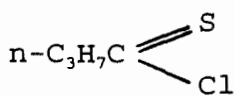
The new process differs from the usual metallisation processes in that the surface of the substrate is activated with a colloidal solution of a hydrated non-noble metal oxide and with an aqueous solution containing a reducing agent.

Stabilisation of these solutions with tin or antimony hydrated oxides and particular urea compounds is disclosed and the inclusion of a small quantity of a reducing agent is suggested to shorten the activation procedure. However, a separate reduction is still required to be utilised and represents a disadvantage of the prior art.

A Document IV represents an item of intervening art which may only be used as prior art for purposes of Art. 54(3). It has an earlier filing date but was published after the present application. It discloses similar colloidal solutions to Document III and discloses a general group of stabilising compounds of formula A



wherein R^1 and R^2 are each selected from a number of substituents. It specifically discloses the use of a compound of formula



together with high concentrations of a reducing agent.

The problem which the invention sets out to solve is therefore to produce an activating composition and an activation process enabling the surface of dielectric substrates to be activated for the purpose of electroless metal deposition without the disadvantages of the known processes.

This problem is solved according to the invention by activating the dielectric substrates with a composition that is free of noble metal salts and which contains a high concentration of reducing agent and thereby enables the activation process to be carried out with the other advantages specified below.

The composition according to the invention consists of an aqueous colloidal solution of a hydrated oxide or of a hydrated oxide mixture of copper, nickel and/or cobalt containing in addition as claim 1.

The colloidal solution preferably contains 15 - 20 mol% of the total quantity of hydrated metal oxides of a hydrated oxide of antimony.

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.

As reducing agents which may be incorporated in the colloidal solution usual reducing agents such as alkali metal borohydride, alkaline-earth metal borohydrides and diethylamino borane may be used, preferably at a concentration of 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 stabilising effect of formula (1) compounds is so pronounced that the colloidal solutions enable the entire metallisation process to be shortened. High concentrations of reducing agent mean separate developer is unnecessary.

The colloidal solution can be prepared using the process described in Document III. In this known process, an aqueous colloidal solution of a hydrated oxide of copper is produced by dissolving a copper salt - particularly a chloride, sulphate, nitrate or acetate of the metal - in an aqueous medium and using a base to bring about precisely-controlled hydrolysis, nucleation and growth.

This gives a hydrated copper oxide which occurs in the form of a colloidal solution because the solubility limit is exceeded. The pH of the aqueous medium is set so as to prevent precipitation of the hydrated oxide, since the oxide particles once precipitated can no longer be returned to the colloidal state. This known colloidal solution is excluded from the protection desired.

For hydrolysis, the base must be added to the aqueous copper salt solution slowly (preferably drop by drop) with stirring at a temperature of 55 - 75°C until a pH of 10.3 - 11.2 is reached. The solution is then allowed to react further under these conditions for 5 - 7 hours. The resulting colloidal solution can be stabilised with suitable stabilisers such as gelatine or gum arabic.

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.

The process for activating a dielectric substrate is characterised in that a wettable substrate is treated with a colloidal solution according to the invention.

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.

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

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.

Comparative Example A, B and C are included for comparison only and do not form part of the present invention. Examples D and E illustrate the invention as claimed.

Comparative 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.

Comparative Example B:

An aqueous colloidal solution was prepared in the same way as in Comparative 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.

Comparative 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 Comparative Example A, with NaOH as the base.

Example D:

A colloidal solution was prepared as in Comparative 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:

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	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:

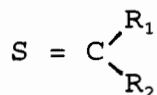
Table

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 and 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

1. Aqueous colloidal solution of a hydrated oxide or of a hydrated oxide mixture of copper, nickel and/or cobalt containing in addition a hydrated oxide of antimony, a stabiliser and a reducing agent and characterised in that the stabiliser is a compound of formula (1)



in which R_1 and R_2 represent an alkyl group with 1-6 carbon atoms or an amino group and in that it has a reducing agent concentration of 1.9 to 2.6 g/l.

2. Colloidal solution as claimed in claim 1 which contains a compound of formula (1) in which R_1 and R_2 represent a methyl or an amino group.
3. Colloidal solution as claimed in claim 1 which contains a compound of formula (1) in which R_1 and R_2 represent amino groups.
4. Colloidal solution as claimed in any one of claims 1 to 3 which contains a compound of formula (1) in a concentration of 0.5 - 2.5 g/l.
5. Process for activating a dielectric substrate, characterised in that a wettable substrate is treated with a colloidal solution according to Claims 1 - 4.

6. Process for producing metallised dielectric substrates by activating the substrate surface, coating with a metal by means of electroless deposition and, as required, electrolytically thickening the thin metal layer, characterised in that the activation is carried out by the process according to Claim 5.

+ Claim 4a.

Colloidal solution as claimed in any one of the preceding claims which contains 15-20 mole % of total metal oxides of the hydrated oxide of antimony, (supported on original p.4, paragraph 1 of description).