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EUROPEAN QUALIFYING EXAMINATION 1990

PAPER B
CHEMISTRY

This paper comprises:

• Instructions to Candidates	90/B(C)/e/1-2
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INSTRUCTIONS TO CANDIDATES

In this paper, you should assume that a European patent appl
for all the Contracting States comprising the appended document
has been filed and that the European Patent Office has communicat
the annexed official letter.

You should accept the facts given in the paper and base your answers upon such facts. Whether and to what extent these facts are used is your responsibility.

You should not use any special knowledge you may have of the subject-matter of the invention, but are to assume that the prior art given is in fact exhaustive.

Your task is now to draft a full response to the official letter. The official letter may or may not necessitate amendment of the description or claims or both and may or may not require arguments, for example as to the relevance of the prior art. You should bear in mind, in drafting your response, that the claims should afford the broadest possible protection. The response should be a letter to the EPO, but no particular form is mandatory. Any amendments should be clearly stated as insertions or deletions in the response or set out in a separate document. In any case, the amendments proposed should be sufficient to meet the requirements of the Convention as to both claims and description.

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* These documents do not necessarily constitute the only or best solution to the task set in Paper A (Chemistry).

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If your response includes a proposal to make any part of application the subject of a divisional application, you sh suggest a text for at least the main claim of the divisional application and also indicate, where appropriate, your grounds fo considering such claim to be acceptable. You need not however propose an introduction for any divisional application.

In addition to your elaborated solution, you may - but this is not mandatory - give, on a separate sheet of paper, the reasons for your choice of solution, for example, why you selected a particular form of claim, a particular feature for an independent claim, a particular piece of prior art as starting point or why you rejected or preferred some piece of prior art. Any such statement should however be brief.

It is assumed that you have studied the examination paper in the language in which you have given your answer. If this is not so, please indicate on the front page of your answer in which language you have studied the examination paper. This always applies to candidates who - after having filed such a request when enrolling for the examination - give their answer in a language other than German, English or French.

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Description

Title: Colloidal solutions of hydrated metal oxides, process for metallising dielectric substrates, and metallised objects obtainable thereby.

5

The invention relates to in part new aqueous colloidal solutions of hydrated metal oxides, activation of dielectric substrates
10 with the said colloidal solutions, coating of the activated substrates by electroless metal deposition, and, where necessary, thickening of the resulting thin metal layer by electrolytic metal deposition, and also to the metallised objects thus obtained, in particular printed electric circuits.

15

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
20 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.

25

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,
30 for instance, the surface is first immersed in a tin(II)chloride solution and, after intermediate rinsing, then immersed in an

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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/dm^2 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.

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 process.

This problem is solved according to the invention by activating the dielectric substrates with a composition that is free of noble metal salts and 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.

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The colloidal solution can be prepared using the process described in Document II. 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,
5 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
10 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.
15

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
20 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
25 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.
30

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
35 adsorbed onto the colloidal particles and produce a change in their charge characteristics. This suppresses the tendency for the particles to coagulate.

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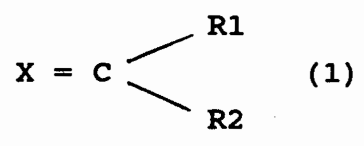
It has been found that stabilisation can be achieved better at a lower concentration of stabilisers, if the colloidal solution also contains a hydrated oxide of antimony, preferably amounting to 15 - 20 mol% of the total quantity of hydrated metal oxides. The production of such colloidal solutions is likewise carried out by the process described in Document II.

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.

A quite specific stabilising effect is shown by 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, in colloidal solutions also containing a hydrated oxide of antimony.

The process for activating a dielectric substrate is characterised in that a wettable substrate is treated with a colloidal solution according to the invention and then, if necessary, following intermediate rinsing with water, treated with a developer solution containing a reducing agent.

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As reducing agents which may be incorporated in the developer solution usual reducing agents such as alkali metal borohydrides, 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 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.

The same reducing agents can be used in the colloidal solution as in the developer solution. 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.

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On the other hand, the concentration of reducing agents in the presence of formula (1) compounds in which X = O 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.

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.

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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
5 mixing thoroughly at 63°C, until a pH of 10.4 was reached. The solution was then allowed to react for 5½ 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.

10

Example B:

An aqueous colloidal solution was prepared in the same way as in Example A, except that the copper acetate solution also contained
15 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:

20 To prepare a colloidal solution, an aqueous solution containing:

$CuCl_2$	7.3 g/l
$SbCl_3$	7.3 g/l
$(NH_2)_2CO$	2.0 g/l
$NaBH_4$	1.4 g/l

25

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

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Example D:

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

5

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

10

Example E:

A colloidal solution was prepared as in Example D, using the compound $(NH_2)_2CS$ instead of CH_3CSNH_2, in an amount of 2.5 g/l.

15

The colloidal solutions in Exaples 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
20 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
25 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:

30

$CuSO_4 . 5H_2O$	15 g/l
EDTA (40%)	68 g/l
NaOH	9 g/l
Tergitol TMN	20 g/l
HCOH (37%)	25 g/l

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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.

5

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

10 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

15 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,

20 adhesion was around 15% less than with colloidal solutions containing hydrated copper oxide.

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

5

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	-

10

15

20 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
25 developing - but also ensures a more uniform quality.

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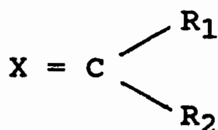
Claims

1. Aqueous colloidal solution of a hydrated oxide or of a hydrated oxide mixture of copper, nickel and/or cobalt, with the exception of a solution of a hydrated oxide of copper.

2. 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.

3. Colloidal solution as claimed in Claim 1 or 2, characterised in that it contains a stabiliser.

4. Colloidal solution as claimed in Claim 2, characterised in that it contains as stabiliser a compound of the following formula (1)



in which X is oxygen or sulphur and R_1 and R_2 represent an alkyl group with 1 - 6 carbon atoms or an amino group.

5. Colloidal solution as claimed in Claim 4, characterised in that it contains a reducing agent.

6. Process for preparing a colloidal solution as claimed in Claims 1 - 5, characterised in that a base is added to a solution containing a salt or mixture of salts of copper, nickel and/or cobalt, and possibly also an antimony salt, at a temperature of 55 -75°C until a pH of 10.3 - 11.2 is obtained, reaction is allowed to take place at this temperature and in this pH range for 5 to 7 hours, and the other components are added as necessary.

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7. Process for activating a dielectric substrate, characteri[illegible] in that a wettable substrate is treated with a colloidal solution according to Claims 1 - 5, including a solution of a hydrated oxide of copper, and then, as required and following intermediate rinsing with water, treated with a developer solution containing a reducing agent.

8. 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 7.

9. Metallised articles, obtainable by the process as claimed in Claim 8.

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Communication

Examination has shown that, for the reasons specified below, the application fails to meet the requirements of the European Patent Convention. You are requested to submit your comments and, where necessary, to file amended application documents.

1. Document III describes aqueous colloidal solutions used to activate dielectric substrates in order to render them suitable for metallisation. They contain a hydrated oxide of copper, iron, nickel or cobalt. The subject-matter of Claim 1 is therefore not new (Article 54(1) and (2) EPC).

   In addition, the aqueous colloidal solutions can contain a hydrated oxide of tin or antimony, a stabiliser, particularly a compound of the formula $RCONH_2$ where $R = NH_2$ or an alkyl group (see in particular the example), and a reducing agent (see also in particular the example). Claims 2 - 5 are therefore not allowable, as they lack novelty.

2. Document IV, an earlier European application, is also relevant to the novelty of the subject-matter of Claims 4 and 5. It describes the use of stabilisers of the formula $RCONH_2$, in which R is an amino group or lower alkyl group, as prior art, and compounds of the formula R_1CSR_2, as stabilisers according to the disclosed invention, in which amongst other possibilities R_1 can be an alkyl group with 1 - 5 carbon atoms and R_2, amongts other possibilities, can be an amino group or an alkyl group with 1 -5 carbon atoms.

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3. The processes claimed in Claims 6, 7 and 8 are also known documents III (cf. in particular the example) and IV (see also in particular the example).

4. The subject-matter of Claim 9 is not new because the process claimed in Claim 8 is known and the metallised objects are the products obtained directly by this known process.

5. If reworded claims are filed, you are asked to bring the description into agreement with them.

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Document III (State of the Art)

This publication concerns a new process for metallising dielectric substrate surfaces, such as plastic or glass surfaces.

5 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. A very thin layer of metal can then be deposited on the activated surface of the substrate 10 using an electroless metallisation bath and subsequently thickened in an electrolytic metallisation bath.

The non-noble metals which can be used in the new process are copper, iron, nickel and cobalt, but copper and nickel are 15 preferred.

The colloidal solutions are prepared by dissolving a salt of one of the aforementioned metals in an aqueous medium and reacting it with a base under very specific reaction conditions (pH: 10.4 - 20 11.3, temperature: ca. 60 - 70°C, reaction time: about 6 hours).

The stability of the colloidal solutions is preferably improved by using stabilisers. Moreover, if the colloidal solutions 25 contain a mixture of a hydrated oxide of the above-mentioned metals and a hydrated oxide of tin or antimony, stabilisation can be achieved with less stabiliser. The activation procedure can thus be somewhat shortened.

30 Those substances normally used to stabilise colloidal solutions, e.g. gelatine and gum arabic, can be employed as stabilisers. However, urea compounds of the formula $RCONH_2$, in which R is an

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amino group or an alkyl group with 1 - 10 carbon atoms, are particularly suitable as stabilisers.

These urea compounds produce such good stabilisation of colloidal solutions containing a hydrated oxide of tin or antimony that a small quantity of a reducing agent can be included in them. In this way the activation procedure can be further shortened.

Example:

NaOH was slowly added with constant stirring at 60°C to an aqueous solution of 0.2 molar $CuCl_2$ and 0.1 molar $SbCl_3$ until a pH of 11.0 was obtained. The solution was then allowed to react for a further 6 hours at 65°C, the pH being kept at 11.0 by addition of NaOH. 2.2 g/l of $(NH_2)_2CO$ and 1.3 g/l of KBH_4 were then added to the resulting colloidal solution.

To activate a substrate made of an ABS copolymer, it was immersed for six minutes in the prepared colloidal solution, rinsed with desalinated water and then treated for five minutes with an aqueous solution containing 1.2 g/l of dimethylamino borane.

The activated substrate was then immersed in a conventional electroless copper-plating bath in order to obtain a thin copper layer of approximately 0.3 μm. The thin copper layer was then thickened in a conventional electrolytic copper-plating bath. The copper layer exhibited excellent adhesion.

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Document IV

Preliminary Note:

Date of filing: prior to the filing date of the present application (i.e. the application currently under examination).
5 Publication: after the filing date of the present application.
Designated Contracting States: the same as in the present application.

European patent application

10

Metallisation of dielectric articles

The invention relates to a new process for activating and metallising the surfaces of dielectric substrates.

15

It is known that dielectric substrates can be rendered suitable for metal-coating by activating them with a colloidal solution of a hydrated mixture of metal oxides, followed by treatment with a so-called developer solution containing a reducing agent.

20

The colloidal solution contains a hydrated oxide or a hydrated oxide mixture of copper, iron, nickel and/or cobalt, a hydrated oxide of antimony, a reducing agent and a stabilising agent of the formula $RCONH_2$, in which R is an amino group or a lower alkyl
25 group.

It has now unexpectedly been found that activation can also be carried out very effectively using an appropriate colloidal solution containing as stabiliser a compound of the formula

30

$$R_1CSR_2 \quad (1)$$

in which R_1 is an alkyl group with 1 - 5 carbon atoms or an aromatic group with 6 - 8 carbon atoms and R_2 is an amino group,
35 an alkyl group with 1 -5 carbon atoms or a halogen atom.

Preferred compounds of the above formula (1) are those containing

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a halogen atom.

The colloidal solution's preparation is in itself known, for example from Document III. Formula (1) compounds are preferably
5 used in a concentration of 0.3 - 2.7 g/l and the reducing agent is preferably used in a concentration of at most 2.2 g/l.

The following example illustrates in more detail the preparation of the colloidal solutions, the activation of the dielectric
10 substrate and the metallisation of the activated substrate.

<u>Example</u>

To produce a colloidal solution, an aqueous solution containing
15

$CuCl_2$	8.0 g/l
$SbCl_3$	8.1 g/l
$n\text{-}C_3H_7C(=S)Cl$	2.0 g/l
$NaBH_4$	2.0 g/l

20

was hydrolysed with NaOH as in the example in Document III.

25 To activate a substrate made of an ABS copolymer, it was immersed for three minutes in the prepared colloidal solution, rinsed with water and then immersed for three minutes in an aqueous solution containing 1.4 g/l of diethylamino borane.

30 The activated substrate was rinsed again with water and treated in a conventional, electroless copper-plating bath. The resulting very thin layer of copper was then thickened in a conventional electrolytic copper-plating bath. The copper layer exhibited better adhesion (measured in accordance with DIN 53 494) than
35 layers produced with known colloidal solutions.

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