EUROPEAN QUALIFYING EXAMINATION 1990

PAPER A
CHEMISTRY

This paper comprises:

INSTRUCTIONS TO CANDIDATES

You are to assume that you have received the annexed letter from your client including a description of an invention for which he wishes you to obtain an European patent together with references to the most pertinent prior art known to your client.

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 to draft an independent claim (or claims) offering the applicant the broadest protection possible while at the same time having a good chance of succeeding before the EPO. In drafting your claim(s) you should bear in mind the need for inventive step over the prior art indicated, the requirements of the Convention as to the form of claims, other requirements of the Convention and the recommendations made in the Guidelines for Examination in the EPO. Dependent claims should be kept to a reasonable number and so drafted as to enable you to fall back upon them should the independent claim(s) fail.

You are also expected to draft an introduction, i.e. that part of the description which precedes the examples or the explanation of the drawings. The introduction should begin with an appropriate title and be sufficient to provide support for all claims. In particular, you should consider the advisability of mentioning advantages of the invention in the introduction.

You are expected to draft claims and an introduction for one European patent application only. If you find that the requirements of the Convention as to unity would in practice cause you to make any of these claims the subject of a separate patent application, you should indicate that separately without further elaboration in this respect.

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.

Client's Letter

We would ask you to file on our behalf a European patent
application concerning the subject-matter described below and
designating all the Contracting States. Please take account of
the state of the art as set out in the two documents annexed.

Research at our company has led to the development of a new
method of metallising dielectric substrates (such as plastics)
and specifically of manufacturing of printed circuits.

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.

With our new process, activation of the substrate's surface - a
prerequisite for deposition and adhesion of the metal layer - is
carried out as follows:

(a) The wettable surface is treated with a colloidal aqueous
    solution of a hydrated oxide or a hydrated oxide mixture of
    copper, nickel and/or cobalt.

(b) Intermediate rinsing with water removes excess colloid.

(c) The substrate's surface is then treated with an aqueous
    developer solution containing a reducing agent. This causes
    the metal ions of the colloid adsorbed 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.

(d) The substrate activated in this way is then rinsed with water
    before undergoing electroless metallisation.

(e) These process steps are usually carried out by immersion.

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.

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.

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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

$$X = C \Big\langle \begin{array}{c} R_1 \\ R_2 \end{array} \qquad (1)$$
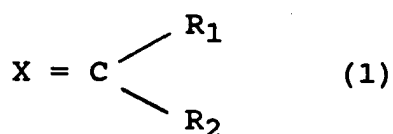
in which X is oxygen or sulphur and R_1 and R_2 are an amino group or an alkyl group with 1 to 6 carbon atoms, have been found to have a quite specific stabilising effect in colloidal solutions also containing a hydrated oxide of antimony.

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.

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 = 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.

Our process 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.

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 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.

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
$(NH_2)_2CO$	2.0 g/l
$NaBH_4$	1.4 g/l

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

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Example D:

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

$$CuCl_2 \qquad 7.3 \ g/l$$
$$SbCl_3 \qquad 7.3 \ g/l$$
$$CH_3CSNH_2 \qquad 1.96 \ g/l$$
$$NaBH_4 \qquad 2.4 \ g/l.$$

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.

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:

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

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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.

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.

The demands made on processes for the manufacture of printed
circuits have given rise to highly developed methods for the
deposition of copper and nickel on plastic surfaces. After
cleaning (if necessary), the wettable plastic surface is first
5 "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
10 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.

15 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
20 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.

It was found that an aqueous colloidal solution of a hydrated oxide of copper can be 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
5 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
10 can no longer be returned to the colloidal state.

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.
15 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.

20 Example

NH_4OH was added drop by drop, with constant stirring, to 500 ml of an aqueous solution of copper sulphate (0.2 mol/l) at a temperature of 64°C until a pH of 10.9 was attained. The
25 temperature of the solution was then raised to 70°C for 6 hours, further NH_4OH being added to maintain the pH at 10.8 - 11.2. The resulting colloidal solution was stabilised by adding 10 g/l of gum arabic.

30 These aqueous colloidal solutions are highly suitable for use as fungicides.