EUROPEAN QUALIFYING EXAMINATION 1991

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 a 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.

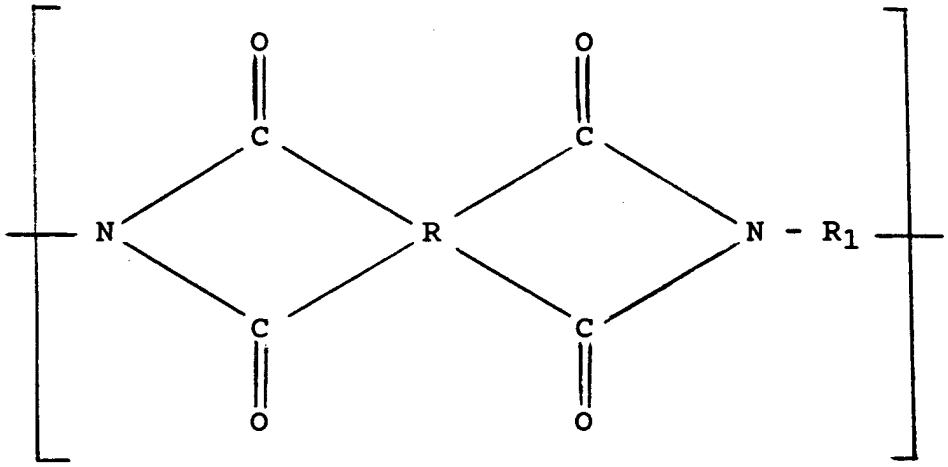
It is assumed that you have studied the examination paper in the language in which you have given your answer. If this is not so, please indicate on the front page of your answer in which language you have studied the examination paper. This always applies to candidates who - after having filed such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

Client's letter

Please file a European patent application on our behalf for the subject-matter described below. When preparing the application, account should be taken of the prior art known from the two documents attached. As far as we are aware, these documents are the most relevant to the subject-matter of the invention.

We are involved in the manufacture of articles, in particular of film and sheets made from polyimides.

We are particularly interested in thermoset cross-linked polyimides in which two imide groups are linked with one or more benzene rings. Such polyimides contain, for example, the following recurring structural units



wherein R is a tetravalent aromatic radical with at least one benzenoid ring and R_1 is a divalent organic radical comprising at least one benzene ring.

In principle, polyimides are manufactured by reacting dianhydrides with diamines and converting the polyamide acids thus obtained into polyimides with the elimination of water and cyclisation.

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Articles made from these polyimides possess excellent physi and chemical properties: they display high strength and heat-resistance and are also highly resistant to attack by a large number of chemicals.

Owing to the considerable strength of polyimides it is, however, difficult to produce shaped articles from them. The tendency is now therefore to produce such structures from the intermediate, that is to say polyamide acids, and only subsequently to convert these into polyimides by heating to the required temperature.

However, the temperature has to be carefully regulated to prevent water produced as water vapour during the conversion of the polyamide into polyimide from being trapped in the compound as it sets. Otherwise, this may result in the formation of voids, which severely reduces the strength of the polyimides. Despite efforts to regulate temperature, it has often been impossible to prevent the occurrence of voids.

We have now developed a process according to which the dehydration and cyclisation of the polyamide acid is brought about using a chemical route. The polyimide is thus formed at a much lower temperature than that temperature needed for the purely thermal heat-treatment method previously used.

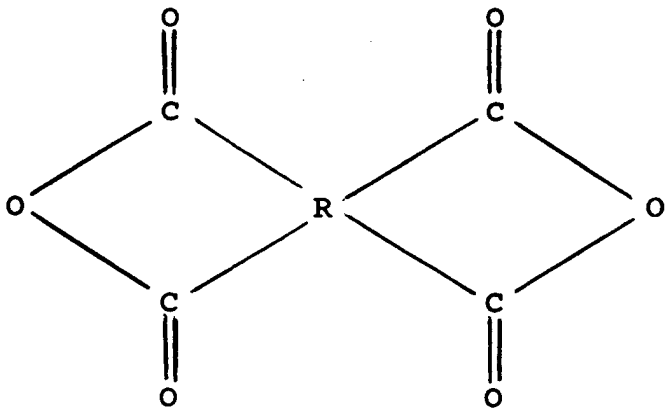
Our process involves the following steps:

A diamine of the structural formula

$$H_2N - R_1 - NH_2$$

wherein R_1 is a divalent radical containing at least one aromatic ring,

is reacted with at least one dianhydride of an aromatic tetracarboxylic acid having the following structural formula



wherein R is a tetravalent radical containing at least one aromatic ring and the four carbonyl groups are attached to different aromatic carbon atoms of R.

The reaction is carried out in a polar organic solvent at a temperature below 120°C. As a minimum temperature 20°C should be maintained. A polyamide acid is formed as intermediate product. This is subsequently converted into polyimide by treatment with an anhydride of a lower aliphatic monocarboxylic acid such as acetic acid anhydride.

The formation of the polyimide could be shown by infrared spectroscopy. With progressive conversion of the polyamide acid a clear shift in the absorption band from 3.1 to 13.85 μm is observed.

In our process, shaped articles are formed from the polyamide acid intermediate prior to conversion to the polyimide, which polyimide is difficult to shape.

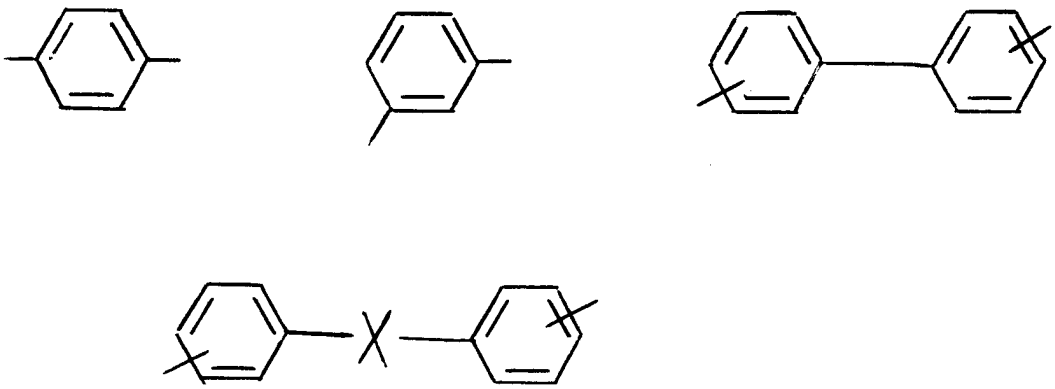
Moulding may take place as soon as the reaction mixture has been partly converted into polyamide acid, for example as soon as a conversion of the reaction mixture of 50% has been achieved.

.../...

To produce the polyamide acid, approximately equimolar amou the said diamine and the dianhydride are mixed as dry solids. mixture obtained is then added, in small proportions and with stirring, to the organic solvent. This method provides good control of the chemical process, which involves an exothermic reaction. The reaction mixture must be stirred until no further increase in the viscosity of the solution is detectable. The polyamide acid content of the solution is then approximately 40%.

Solutions with a small polyamide acid content (less than 15% by weight) - which are not suitable for the manufacture of shaped articles - can be used as coating compositions. They may be used to coat metal objects such as sheets or wires, and woven plastics. Subsequent treatment with the aliphatic carboxylic acid anhydride produces a polyimide film.

The aromatic radical designated R_1 in the structural formula for the diamine may consist of one of the following groups



wherein X is an alkylene group with 1 to 3 carbon atoms, sulphur, SO_2 or oxygen.

Among the diamines which are particularly suitable are those wi
two rings, for example:

benzidine
4,4'-diamino-diphenyl methane
4,4'-diamino-diphenyl propane
4,4'-diamino-diphenyl ether
4,4'-diamino-diphenyl sulphide
4,4'-diamino-diphenyl sulphone.

When the latter two diamines are used, the compounds produced display particularly good properties, in particular the films made from them have excellent tensile strength.

Examples of aromatic tetracarboxylic acid dianhydrides of the above formula are in particular:

pyromellitic acid dianhydride (1, 2, 4, 5-benzene tetracarboxylic acid dianhydride)
2,3,6,7-naphthalene tetracarboxylic acid dianhydride
3,3',4,4'-diphenyl tetracarboxylic acid dianhydride
3,4,3',4'-benzophenone tetracarboxylic acid dianhydride.

The polar solvent used in the polymerisation process must dissolve, but not react with, at least one of the reactants. The solvent selected should preferably also act as a solvent for the polyamide acid intermediate formed.

Solvents that meet these requirements particularly well are

N,N-dimethylformamide and
N,N-dimethylacetamide.

These two solvents may easily be removed by evaporation from the reaction products formed.

Apart from acetic acid anhydride, mentioned above, one can use as dehydrating and cyclising agents for the polyamide acid formed from the reaction, propionic acid anhydride, butyric acid anhydride and isobutyric acid anhydride and mixtures thereof.

It is advantageous to add a diluent to the anhydride. In this way a better diffusion of the anhydride through the polyamide acid structure is achieved. Mostly benzene is used as diluent but cyclohexane, carbon tetrachloride or acetonitrile may also be used.

It is also highly desirable to add to the anhydride of the lower aliphatic carboxylic acid a tertiary amine such as pyridine, 4-benzylpyridine, 3,4-lutidine or isoquinoline. The tertiary amine acts as a catalyst for the conversion of the polyamide acid into polyimide. It largely prevents the polymer from being degraded by hydrolysis and promotes ring closure. The tertiary amine, such as pyridine, may be used in such a quantity that its molar proportion to the anhydride is 1:1.

Among the particularly effective amines are trimethylamine and triethylamine. These accelerate the conversion of the polyamide acid to the polyimide even more effectively than pyridine. Smaller quantities than used for pyridine are exceptionally effective.

Shaped polyimide articles which can advantageously be produced by our process are, in particular, self-supporting films or sheets. By extrusion of the viscous polyamide acid solution films can be produced that are subsequently passed through an acid anhydride bath where conversion to polyimide by cyclisation occurs. The polyimide films are flexible and tear-resistant.

According to another procedure, a solution of polyamide acid is cast on a support having a smooth surface, for example a glass plate, and the viscous solution is spread over the support with a doctor blade to form a thick film. The coated support is then, for example, immersed in an acetic acid anhydride bath where dehydration and cyclisation of the polyamide acid to the polyimide occurs.

It was found that the film removed from the support showed an asymmetric structure with a thin, slightly-porous skin and a thicker, porous layer. The skin was the top layer which had been directly exposed to the cyclising solution, while the porous layer was the side face-down on the support.

The microporous sheet produced had selective permeability properties. It proved to be highly suitable for use as a semipermeable membrane for the separation of mixtures of liquids or gases in reverse osmosis or ultrafiltration.

The membrane should be between 100 and 300 μm thick, since a thinner membrane has insufficient strength in many instances while a thicker membrane is often insufficiently permeable to the solvent.

A number of examples illustrating the process of the invention follows.

Example 1

14g of benzidine and 14g of pyromellitic acid dianhydride were mixed in the dry state and dissolved portionwise in 70 ml of dimethylacetamide with continuous stirring. Another 20 ml of dimethylacetamide was added, and after the diamine had reacted with the acid anhydride a polyamide acid solution with a polymer content of 22% by weight was obtained. The viscous solution of polyamide acid was moulded by extrusion into a self-supporting film which was immersed for 10 hours in a solution of 180 ml benzene, 80 ml acetic acid anhydride and 40 ml pyridine. The film was then vacuum-dried with heating at a temperature of 110°C. Infrared spectral analysis indicated that the film was of polyimide. It was flexible but tear-resistant.

Example 2

The procedure was essentially the same as for Example 1 but no pyridine was added to the acetic acid anhydride solution. In this instance, conversion of the polyamide acid to polyimide took 15 hours.

Example 3

4,4'-Diamino-diphenyl propane, 12g, and pyromellitic acid dianhydride, 17 g, were mixed to form a powdered mixture which was then added to 75 ml of dimethylformamide with continuous stirring and with cooling. Another 30 ml of dimethylformamide was added so that a polyamide acid solution with a polymer component of 24.5% by weight resulted. Films produced from the solution were immersed in a solution consisting of 200 ml of benzene and 50 ml of acetic acid anhydride and to which 30 ml of pyridine had also been added. After an immersion time of 11 hours, the conversion of the polyamide acid to the polyimide was complete.

Example 4

A film produced from a polyamide acid solution in a similar manner to Example 3 was immersed in a solution containing 200 ml benzene and 50 ml acetic acid anhydride to which solution 18 ml of triethylamine had been added as tertiary amine. After an immersion time of 6 hours, that is, after a much shorter period than in Example 3, the conversion of the polyamide acid to the polyimide was complete.

Example 5

A mixture of 4,4'-diamino-diphenyl sulphone, 12g, and pyromellitic acid dianhydride, 10 g, was added portionwise with continuous stirring and with cooling to 30 ml of dimethylformamide. Another 20 ml of dimethylformamide was then added. Reaction of the constituents produced a polyamide acid solution with a polymer content of 22% by weight. As in the previous examples, this was used to produce a self-supporting film which was immersed in a bath consisting of 15 parts cyclohexane, 1 part pyridine and 1 part acetic acid anhydride for 10 hours and then vacuum-dried at 120°C. The film proved to be highly tear-resistant.

Example 6

4,4'-diamino-diphenyl ether, 16 g, and pyromellitic acid dianhydride, 18 g, were reacted in dimethylacetamide as solvent to form a solution of polyamide acid (20% by weight). More dimethylacetamide was used to dilute the solution to a solids content of 10%, and the solution was then spread on a glass plate with a doctor blade to produce a 0.5 mm thick film. The glass plate supporting the film was immersed in a benzene solution containing 1 mole/l of pyridine and 1 mole/l of acetic acid anhydride. After being immersed for 10 hours in the solution, which was heated to 70°C, the film had become cloudy. Having been

cyclised to polyimide the film was then removed from the gl plate, washed with benzene and dried at 80°C. The film produc was 0.3 mm thick and of asymmetric structure with a shiny, slightly porous skin on top and, underneath, a matt, fairly porous, thicker layer which had been face-down on the glass plate during cyclisation.

Example 7

Another sheet was produced in a similar manner to Example 6, the difference being that 4,4'-diamino-diphenyl sulphide, 16 g, was used as the diamine. Again, a sheet with an asymmetric structure was obtained, but it showed a better tear-resistance than the membrane obtained in the previous example, presumably due to the diamine used.

The sheets of asymmetric structure obtained in Examples 6 and 7 showed selective permeability properties to gases and liquids and proved to be highly suitable for use as microporous membranes.

The following table gives a summary of the properties of the films produced in Examples 1 to 7.

Example	Modulus of elasticity in MPa	Tensile strength in MPa	Elongation in %
1	2400	98	7
2	2480	102	9
3	2270	94	6
4	2300	100	8
5	3800	142	15
6	2670	112	8
7	3680	138	14

Document I (State of the Art)

The invention relates to a process for preparing polyimides in which approximately equimolar amounts of pyromellitic acid dianhydride and a diamine of the following structural formula: $H_2N-R-NH_2$, wherein R is a divalent group of an aromatic radical, are reacted in an organic solvent. For example, one can add slowly a solution of one of the reaction components to a solution of the other reaction component. With solid reaction components a dry mixture of the two components may first be prepared and this added slowly to the solvent.

The reaction mixture is kept at a temperature below 60°C, producing a viscous solution containing at least 50% polyamide acid which is then heated to between 350 and 550°C, so that the polyamide acid is converted to the polyimide.

Example 1

m-Phenylenediamine, 20 g, was dissolved in 150 ml of dimethylsulphone. 22 g of pyromellitic acid dianhydride was added to this solution with cooling of the solution. After some time a viscous solution was obtained. 50 ml of dimethylsulphone was then added to obtain a readily pourable solution with approx. 14% by weight of polyamide acid. Films were formed from this solution

which films were then deposited on thin steel plates, dried nitrogen at 120°C and then heated to 400°C in an oven to conv the polyamide acid into the polyimide.

The polyimide films produced in this way can be used in particular as high-grade packaging material and, for example, for electrical cable wrappings.

Example 2

Other films were produced in a similar manner, 4,4'-diamino-diphenyl ether being used as the diamine.

After the polyamide acid films had been heated to 450°C, tough polyimide films were again obtained.

Document II (State of the Art)

A process for preparing polyimides by reacting pyromellitic acid dianhydride with an aromatic diamine, the reaction being carried out in two stages. In a first stage, a condensation reaction in the presence of an organic solvent produces a soluble pyromellitic amide acid which, in a second stage, is converted by heating and with the elimination of water into a thermally stable polypyromellitic imide. Heating to 400°C is necessary to achieve total conversion.

The aromatic polyimides thus obtained have good heat-resistance. They show, however, poor processability or mouldability, so that it is very difficult to mould the polyimide as such.

In the process of the invention, a polyamide acid powder containing up to 80% by weight is compacted by pressure of 15 to 60 N/mm^2, and the compacted material is then sintered at a temperature of 250 to 400°C and under a pressure of 14 to 21 N/cm^2. Pressure and temperature values must be carefully selected so as to enable the water to escape from the compacted material.

Example

Pyromellitic acid dianhydride was reacted with para-phenylenediamine at 120°C to produce polyamide acid. A mould charge of the powdered acid was compacted to a shape 8.30 mm thick in a mould using a cylindrical stamp at a pressure of 47 N/mm^2. The compacted disc was sintered in an oven at 350°C under a pressure of 17.5 N/cm^2 with simultaneous conversion into polypyromellitic imide.