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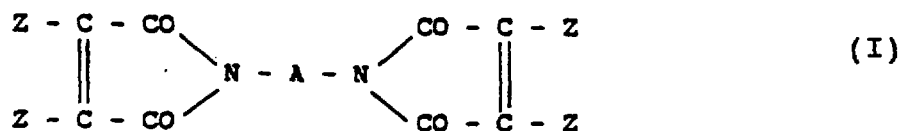
The present invention relates to new heat-resistant polymers whose production involves, besides other optional reactants, bis(maleimides) optionally including a bis(maleimide) containing a diorganopolysiloxane group in its structure and aromatic diamines. It also relates to processes for preparing these polymers.

It is known (see French Patent FR-A-1,555,564) that heat-resistant polymers may be obtained by reacting an N,N'-bis(imide) of an unsaturated dicarboxylic acid, such as, for example, an N,N'-bis(maleimide), with certain aromatic diprimary diamines. These polymers, which show exceptional heat resistance, may be used for the manufacture of moulded parts or laminates, with a view to the widest diversity of applications.

It has now been found that polymers can be obtained possessing, among other properties, a high impact strength, by reacting one or more N,N'-bis(maleimides) of the type described in the abovementioned patent with one or more aromatic diprimary diamines in the presence of an N,N'-bis(maleimide) containing a diorganopolysiloxane group in its structure and optionally of another copolymerisable reactant and/or a catalyst.

More specifically, the present invention relates to polymers containing imide groups, characterised in that they comprise the product of reaction, at a temperature ranging from 50°C to 300°C, between:

(a) an N,N'-bis(maleimide) or a combination of several bis(maleimides) of formula:

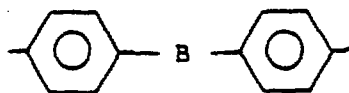


in which:

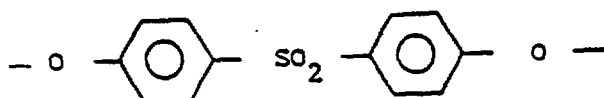
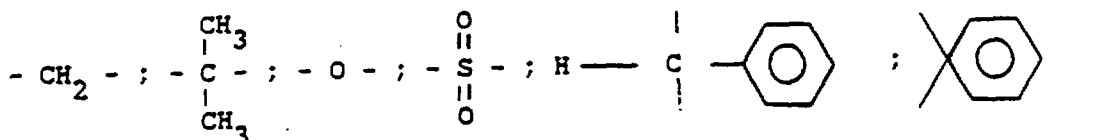
the symbols Z, which may be identical or different, each denote H, CH₃ or Cl;

the symbol A denotes a divalent radical chosen from the group consisting of the following radicals:

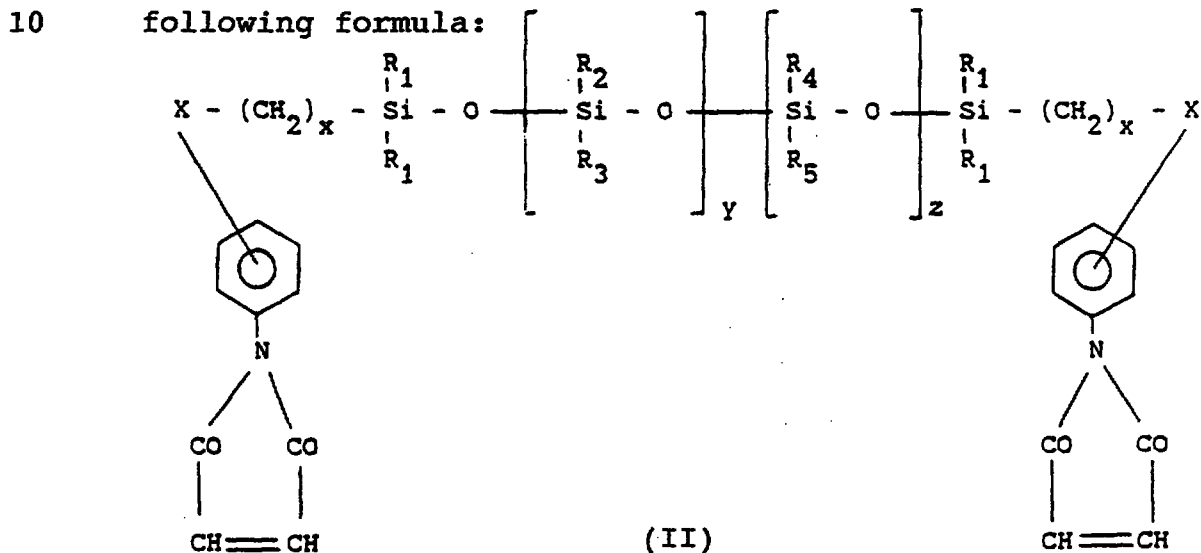
cyclohexylenes; phenylenes, 4-methyl-1,3-phenylenes (sic); 2-methyl-1,3-phenylene; 5-methyl-1,3-phenylene; 2,5-diethyl-3-methyl-1,4-phenylene; and the radicals of formula:



5 in which B denotes a single valency bond or a group:

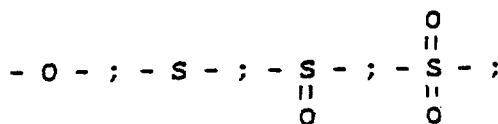


(b) an N,N'-bis(maleimide) containing a diorgano-polysiloxane group corresponding essentially to the following formula:



15 in which:

X, which is in the ortho, meta or para position with respect to the carbon atom of the benzene ring linked to the nitrogen, denotes one of the following atoms or groups:



20

R_1 , R_2 , R_3 , R_4 and R_5 , which may be identical or

different, each denote a monovalent hydrocarbon radical chosen from: linear or branched alkyl radicals having from 1 to 12 carbon atoms, it being possible for these radicals to be substituted with one or more chlorine, bromine or fluorine atoms or with a -CN group; a phenyl radical optionally substituted with one or more alkyl and/or alkoxy radicals having from 1 to 4 carbon atoms or with one or more chlorine atoms;

the symbol X (sic) is an integer falling within the range from 2 to 8;

the symbols y and z denote numbers, which may be identical or different, integral or fractional, whose sum falls within the range from 0 to 100;

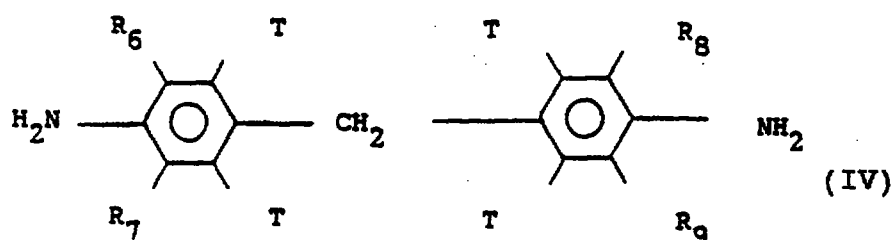
(c) one or more diprimary diamines selected from the group composed of:

*(c1) the species corresponding to the general formula:



in which the symbol E denotes one of the divalent radicals denoted by the symbol A of the formula (I), it being possible for the symbols A and E present in the same polymer to be identical to or different from one another;

*(c2) the species corresponding to the general formula:

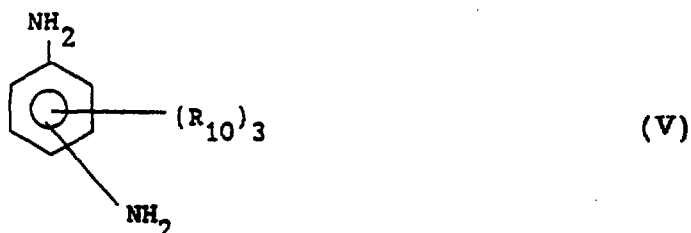


in which:

the symbols R_6 , R_7 , R_8 and R_9 , which may be identical or different, each denote a methyl, ethyl, propyl or isopropyl radical;

the symbols T, which may be identical or different, each denote a hydrogen atom or a chlorine atom; and

*(c3) the species corresponding to the general formula:



in which:

the amino radicals (lacuna) in the meta or para position with respect to one another;

5 the symbols R_{10} , which may be identical or different, each denote a methyl, ethyl, propyl or isopropyl radical;

(d) optionally, one or more monomers other than a bis(maleimide) of formula (I) or of formula (II) and
10 containing one or more polymerisable carbon-carbon double bonds; and

(e) optionally, a catalyst.

By way of specific examples of bis(maleimides) of formula (I), there may be mentioned in particular:

15 N,N' -(meta-phenylene)bis(maleimide),
 N,N' -(para-phenylene)bis(maleimide),
 N,N' -(4,4'-diphenylmethane)bis(maleimide),
 N,N' -(4,4'-diphenyl ether)bis(maleimide),
 N,N' -(4,4'-diphenyl sulphone)bis(maleimide),
20 N,N' -(1,4'-cyclohexylene)bis(maleimide),
 N,N' -[4,4'-(1,1-diphenylcyclohexane)]bis(maleimide),
 N,N' -[4,4'-(2,2-diphenylpropane)]bis(maleimide),
 N,N' -(4,4'-triphenylmethane)bis(maleimide),
25 N,N' -(2-methyl-1,3-phenylene)bis(maleimide),
 N,N' -(4-methyl-1,3-phenylene)bis(maleimide),
 N,N' -(5-methyl-1,3-phenylene)bis(maleimide).

These bis(maleimides) may be prepared according to the processes described in US Patent US-A-3,018,290
30 and British Patent GB-A-1,137,290. For the implementation of the present invention, N,N' -(4,4'-diphenylmethane)bis-maleimide), taken alone or mixed with N,N' -(2-methyl-1,3-phenylene)bis(maleimide), N,N' -(4-methyl-1,3-phenylene)-bis(maleimide) (sic) and/or N,N' -(5-methyl-1,3-phenyl-
35 ene)bis(maleimide), is preferably used.

In relation to the bis(maleimide)-siloxanes of formula (II), when y and/or z are greater than 1, the compound in question is polymeric in structure and is rarely a single compound, but most often a mixture of compounds of the same chemical structure which differ in the number of repeated units in their molecule; this leads to an average value of y and/or z which may be integral or fractional.

When the preparation of the polymers according to the invention is performed, according to the directions given below, in an organic solvent or diluent, it is possible to use any one of the compounds of the formula (II).

As bis(maleimides) that are preferred as representative, there may be mentioned those which correspond to the formula (II) in which:

1. $X = - O -$; R_1, R_2, R_3, R_4 and R_5 , which may be identical or different, each denote a linear or branched alkyl radical having from 1 to 6 carbon atoms; $x = 2, 3, 4$ or 5 ; and $y + z$ falls within the range from 0 to 100, and preferably from 4 to 70.

2. $X = - O -$; R_1, R_2 and R_3 , which may be identical or different, each denote a linear or branched alkyl radical having from 1 to 6 carbon atoms; R_4 and R_5 each denote a phenyl radical; $x = 2, 3, 4$ or 5 ; and $y + z$ falls within the range from 0 to 100, and preferably from 4 to 70.

3. $X = - O -$; R_1, R_2 and R_4 , which may be identical or different, each denote a linear or branched alkyl radical having from 1 to 6 carbon atoms; R_3 and R_5 each denote a phenyl radical; $x = 2, 3, 4$ or 5 ; and $y + z$ falls within the range from 0 to 100, and preferably from 4 to 70.

4. $X = - O -$; R_1 denotes a linear or branched alkyl radical having from 1 to 6 carbon atoms; R_2, R_3, R_4 and R_5 each denote a phenyl radical; $x = 2, 3, 4$ or 5 ; and $y + z$ falls within the range from 0 to 100, and preferably from 4 to 70.

As bis(maleimides) that are still more preferred

as representative, there may be mentioned those which correspond to the formula (II) in which:

5 5. $X = - O -$; $R_1 = R_2 = R_3 = R_4 = R_5$ = linear alkyl radical having from 1 to 3 carbon atoms; $x = 2, 3$ or 4 ; and $y + z$ falls within the range from 0 to 100, and preferably from 4 to 70.

10 6. $X = - O -$; $R_1 = R_2 = R_3$ = linear alkyl radical having from 1 to 3 carbon atoms; $R_4 = R_5$ (lacuna) phenyl radical; $x = 2, 3$ or 4 ; and $y + z$ falls within the range from 0 to 100, preferably from 4 to 70.

7. $X = - O -$; $R_1 = R_2 = R_4$ = linear alkyl radical having from 1 to 3 carbon atoms; $R_3 = R_5$ = a phenyl radical; $x = 2, 3$ or 4 ; and $y + z$ falls within the range from 0 to 100, preferably from 4 to 70.

15 8. $X = - O -$; R_1 = linear alkyl radical having from 1 to 3 carbon atoms; $R_2 = R_3 = R_4 = R_5$ = phenyl radical; $x = 2, 3$ or 4 ; and $y + z$ falls within the range from 0 to 100, preferably from 4 to 70.

20 As bis(maleimides) which are most especially representative, there may be mentioned those which correspond to the formula (II) in which:

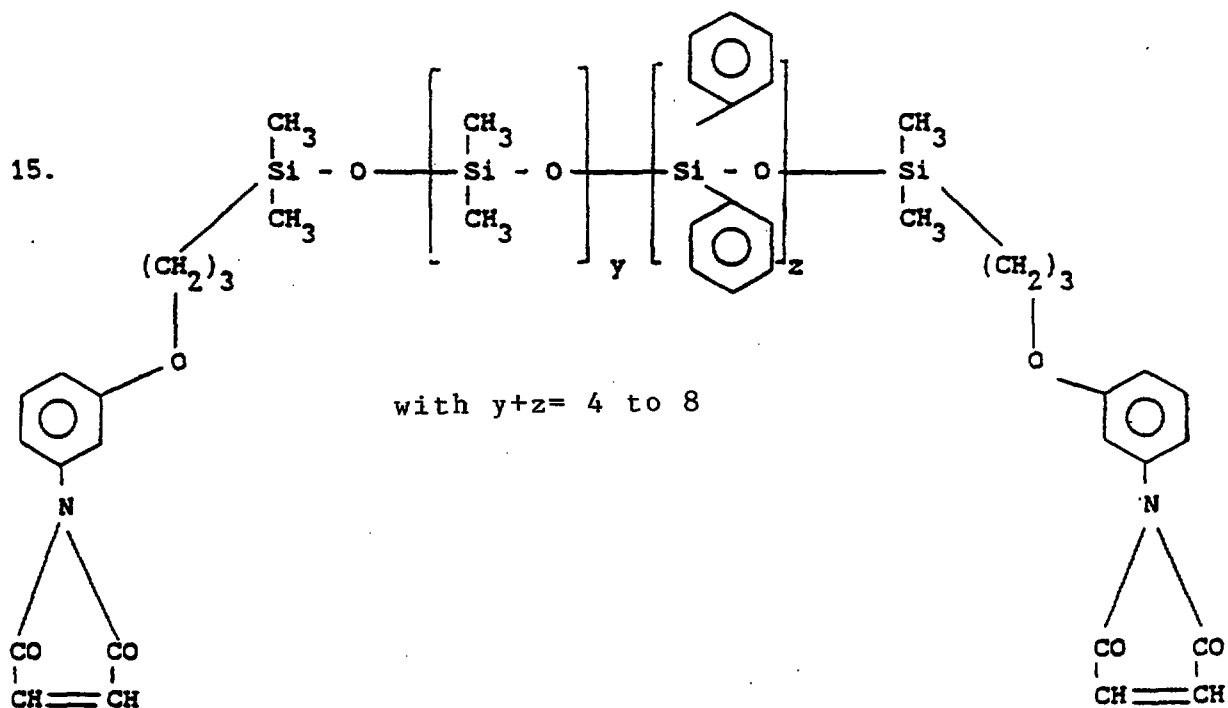
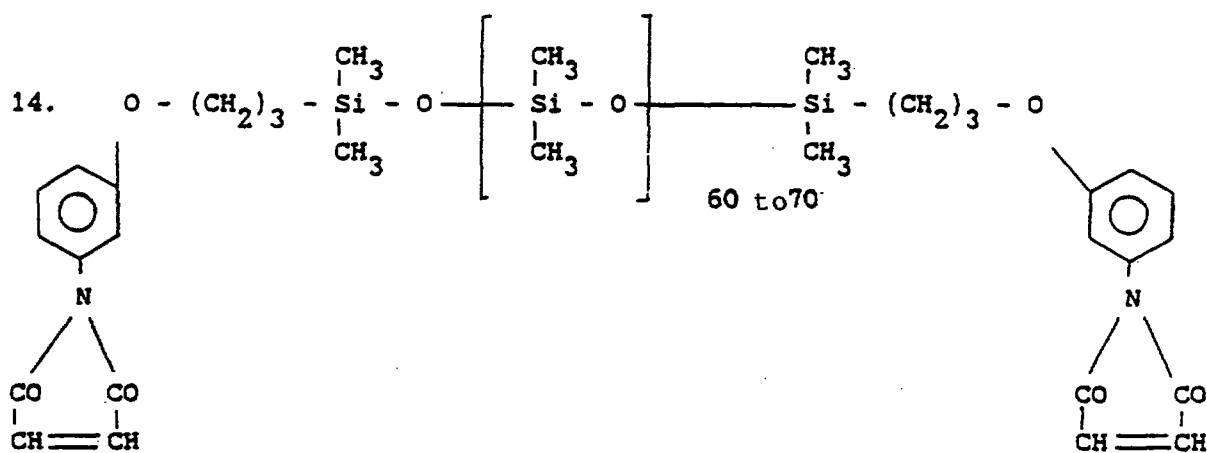
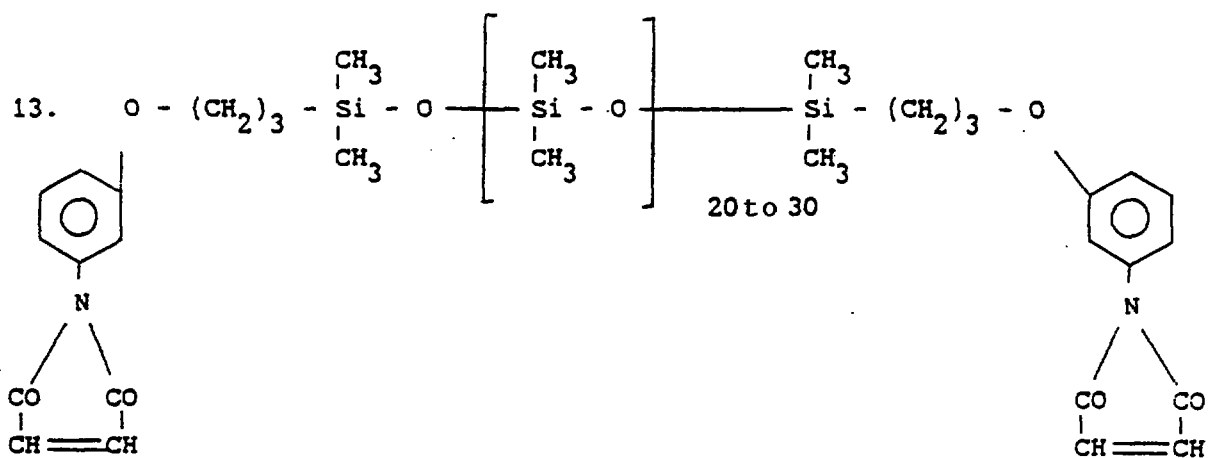
9. $X = - O -$; $R_1 = R_2 = R_3 = R_4 = R_5$ = methyl radical; $x = 3$; and $y + z$ falls within the range from 0 to 100, preferably from 4 to 70.

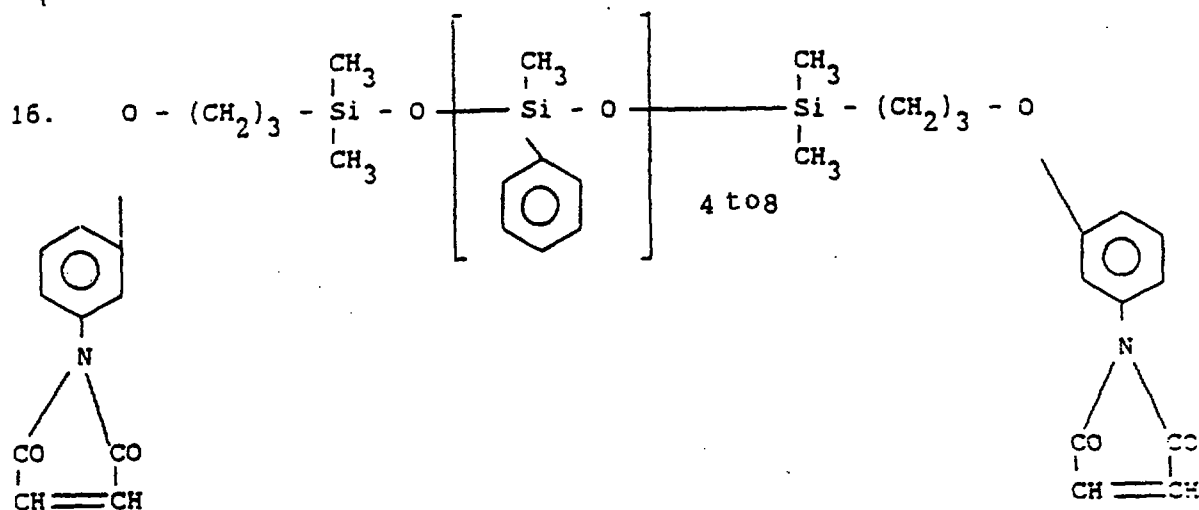
25 10. $X = - O -$; $R_1 = R_2 = R_3$ = methyl radical; $R_4 = R_5$ = phenyl radical; $x = 3$; and $y + z$ falls within the range from 0 to 100, preferably from 4 to 70.

30 11. $X = - O -$; $R_1 = R_2 = R_4$ = methyl radical; $R_3 = R_5$ = phenyl radical; $x = 3$; and $y + z$ falls within the range from 0 to 100, preferably from 4 to 70.

12. $X = - O -$; R_1 = methyl radical; $R_2 = R_3 = R_4 = R_5$ = phenyl radical; $x = 3$, and $y + z$ falls within the range from 0 to 100, preferably from 4 to 70.

35 As specific examples of bis(maleimide)-siloxanes which are most especially representative, the following will be mentioned in particular:





5 When the preparation of the polymers according to the invention is performed as a bulk polymerisation, it is preferable to use as bis(maleimides) of formula (II) those in which the diorganopolysiloxane group contains a plurality of Si-phenyl or Si-(substituted phenyl) bonds. Bis(maleimides) of this type which are suitable are those belonging to the following groups, classified in increasing order of preference:

- bis(maleimides) Nos. 2, 3 and 4;
- bis(maleimides) Nos. 6, 7 and 8;
- bis(maleimides) Nos. 10, 11 and 12.

15 Among the bis(maleimides) belonging to these preferred groups, those which are most especially suitable for the bulk preparation of the polymers are the compounds in which the ratio:

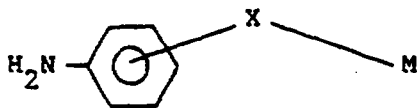
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$$\frac{\text{number of Si-phenyl (optionally substituted) bonds}}{\text{number of Si-alkyl bonds}}$$

is equal to at least 0.25; by way of specific examples of bis(maleimides) of this type, reference will be made, in particular, to the compounds (sic) No. 16.

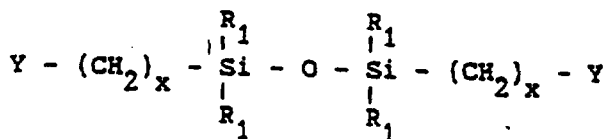
25 The bis(maleimides) of formula (II) are novel compounds which are obtained by reacting maleic anhydride, in the presence of a dehydrating agent, a tertiary amine, an organic diluent and a catalyst, with a diamine containing a diorganopolysiloxane group of formula:

5 in which $X, R_1, R_2, R_3, R_4, R_5, x, y$ and z have the meanings given above for the formula (II).

According to these documents, a first method for preparing these diamines, which is applicable especially when a compound of the formula (VI) in which $y = z = 0$ can be obtained, that is to say when a diamine containing a diorganodisiloxane group can be obtained, consists in reacting a compound of formula

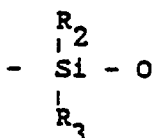


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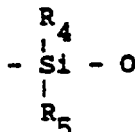


where x has the value indicated above and Y is a chlorine, bromine or iodine atom, working at a temperature between 20° and 200°C in the presence of an aprotic polar solvent.

5 In the case where it is desired to obtain a diamine of formula (VI) in which y and/or z are other than zero, a second preparation method taught by these documents consists in copolymerising one mole of diamine containing a diorganopolysiloxane group, prepared as
10 stated above, with a quantity of one or more cyclic diorganopolysiloxanes capable of giving y moles of siloxy groups of formula:

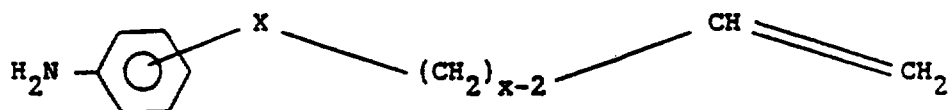


and/or z moles of siloxy groups of formula:

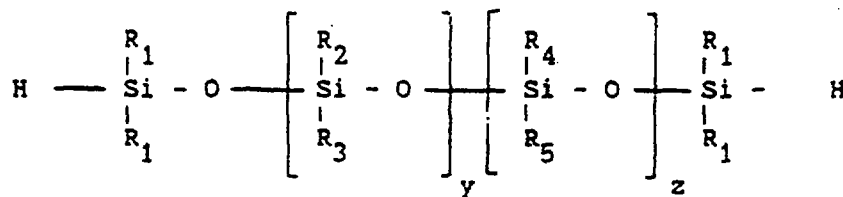


15 In general, the reaction proceeds at a temperature of between 80° and 250°C in the presence, in this instance also, of a solvent and optionally of a suitable catalyst.

20 Another way of preparing the diamines of formula (VI), with y and/or z being equal to zero or other than zero, is to react an ethylenically unsaturated compound of formula:

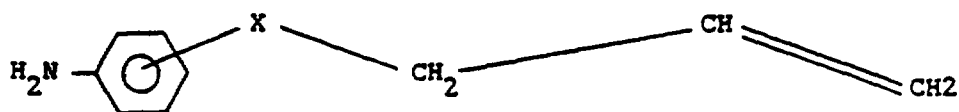


25 in which X, which is in the ortho, meta or para position with respect to the carbon atom of the benzene ring linked to the nitrogen, and x have the meanings given above, with an alpha,omega-bis(hydrogeno)diorganopolysiloxane of formula:



in which R_1 , R_2 , R_3 , R_4 , R_5 , y and z have the meanings given above. This hydrosilylation reaction is performed by working in bulk in the absence of solvent, and using a platinum-based catalyst. The alpha,omega-bis(hydrogeno)diorganopolysiloxanes employed are products that are well known in the silicone industry, and are in some cases commercially available. They are described, for example, in French Patents FR-A1-2,486,952 and FR-A5-2,058,988.

When it is decided to employ this hydrosilylation reaction for preparing a diamine of formula (VI), the ethylenically unsaturated amino substrate which is very suitable for reacting with the alpha,omega-bis(hydrogeno)diorganopolysiloxane consists, in particular, of an allyloxylaniline of formula:



Under these favourable conditions, the products are hence diamines of formula (VI) which will serve to manufacture some bis(maleimides) of formula (II), that is to say those in which $\text{X} = - \text{O} -$, $x = 3$ and R_1 , R_2 , R_3 , R_4 , R_5 , y and z have the general or specific meanings given above.

To return to the process for preparing the bis(maleimides) of formula (II), the diamine of formula (VI) is reacted, as stated above, with maleic anhydride in the presence of a dehydrating agent, a tertiary amine, an organic diluent and a catalyst.

The maleic anhydride is used in quantities at least equal to one mole per available NH_2 group; larger quantities are generally used, namely of the order of

1.01 to 1.5 moles per available NH_2 group.

As dehydrating agent, it is advantageous to use a lower carboxylic acid anhydride such as acetic anhydride, in quantities at least equal to one mole per available NH_2 group present in the molecule of diamine of formula (VI) introduced. Larger quantities are generally used, namely of the order of 1.05 to 1.5 moles per available NH_2 group.

Among suitable tertiary amines, there may be mentioned, in particular, trialkylamines as well as N,N-dialkylanilines in which the alkyl radicals have from 1 to 12 carbon atoms. Triethylamine and N,N-dimethylaniline are advantageously used. The quantities of tertiary amine are generally between 0.05 and 0.8 mole per available NH_2 group.

The reaction is performed in a liquid organic diluent under the working conditions, in practice between 20° and 100° at atmospheric pressure. Among usable diluents, preference will be given to those which dissolve the starting maleic anhydride under the temperature conditions adopted for the reaction and in the presence of the other constituents of the reaction mixture.

Among these, the following may be mentioned in particular:

hydrocarbons such as benzene, toluene and cyclohexane,
chlorinated derivatives such as chlorobenzene or methylene chloride,
cyclic or acyclic ethers such as tetrahydrofuran, dioxane or ethyl ether,
dialkyl ketones such as acetone or methyl ethyl ketone.

As catalysts, it is possible to use a nickel derivative which is soluble in the liquid phase of the reaction mixture, such as, for example, nickel salts of carboxylic acids, optionally hydrated, as well as the chelated forms of this metal. The acetate and acetylacetonate are especially suitable. These catalysts are employed in very small quantities, of the order of

0.5 $\times 10^{-3}$ to 5 $\times 10^{-3}$ moles per mole of available NH_2 group.

In practice, for carrying out the process, the first step is to react maleic anhydride and the diamine of formula (VI), working in the chosen diluent at a temperature ranging from 30°C to 100°C for a time ranging, according to the temperature, from a few minutes to 1 hour. The dehydrating agent, the tertiary amine and finally the catalyst are then added to the reaction medium, and the mixture is thereafter left to react under the temperature conditions previously adopted for a period ranging, according to the temperature, from 1 hour to 3 hours. In general, the reaction is terminated by adding a non-solvent such as water, and the bis(maleimide) of formula (II) prepared is isolated according to the usual methods.

By way of specific examples of diamines (c1) of formula (III), there may be mentioned in particular:

para-phenylenediamine,
meta-phenylenediamine,
4,4'-diaminodiphenylmethane,
2,2-bis(4-aminophenyl)propane,
benzidine,
bis(4-aminophenyl)ether,
4,4'-diaminediphenyl (sic) sulphone,
and mixtures thereof.

For implementing the present invention, 4,4'-diaminodiphenylmethane is preferably used.

By way of specific examples of hindered diamines (c2) and (c3) of formulae (IV) and (V), there may be mentioned in particular:

4,4'-diamino-3,3',5,5'-tetramethyldiphenylmethane,
4,4'-diamino-3,3',5,5'-tetraethyldiphenylmethane,
4,4'-diamino-3,5-dimethyl-3',5'-diethyldiphenylmethane,
4,4'-diamino-3,3'-diethyl-5,5'-dimethyldiphenylmethane,
4,4'-diamino-3,3',5,5'-tetraisopropyldiphenyl-

methane,
 4,4'-diamino-3,3'-diisopropyl-5,5'-dimethyldi-
 phenylmethane,
 4,4'-diamino-2,2'-dichloro-3,3',5,5'-tetraethyl-
 diphenylmethane,
 1,3-diamino-2,4-diethyl-6-methylbenzene,
 1,3-diamino-2-methyl-4,6-diethylbenzene,
 and mixtures thereof.

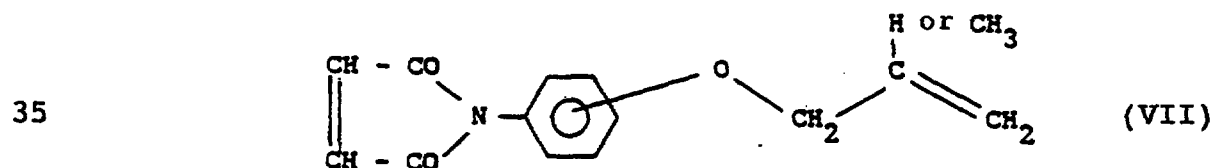
These hindered diamines may be prepared according
 to the processes described in British Patent GB-A-852,651
 and US Patent US-A-3,481,900. For implementing the
 present invention, 4,4'-diamino-3,3',5,5'-tetraethyl-
 diphenylmethane, 4,4'-diamino-3,3'-diethyl-5,5'-dimethyl-
 diphenylmethane and mixtures thereof are preferably used.

With respect to the polyimides obtained according
 to French Patent FR-A-1,555,564 by heating, in particular
 N,N'-(4,4'-diphenylmethane)bis(maleimide) and an aromatic
 diamine, it has been found that the addition of an N,N'-
 bis(maleimide) containing a diorganopolysiloxane group of
 formula (II) to the polymerisation medium is a measure
 which makes it possible, in particular, to facilitate,
 during the bulk preparation of these polymers, the
 conversion of the maleimides to the molten state, and to
 improve the mechanical properties markedly by multiplying
 at least 1.5-fold the resilience values of the cured
 polymers.

It may be advantageous in some cases to modify
 the polymers according to the present invention by
 employing a copolymerisable reactant (d). As an optional
 reactant (d) which is very suitable, the following may be
 mentioned in particular:

*when it is desired, for example, to lower the
 fluidity of the polymerisation medium:

(d₁) either one or more monomers of formula:

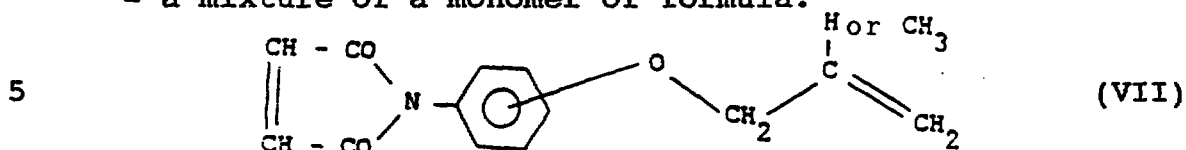


in which the allyloxy or methallyloxy radical is in the

ortho, metha (sic) or para position with respect to the carbon atom of the benzene ring linked to the nitrogen;

(d₂) or a compound comprising:

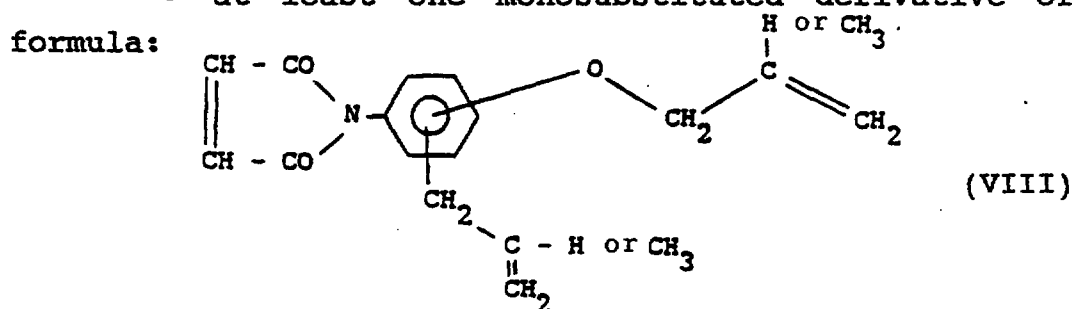
- a mixture of a monomer of formula:



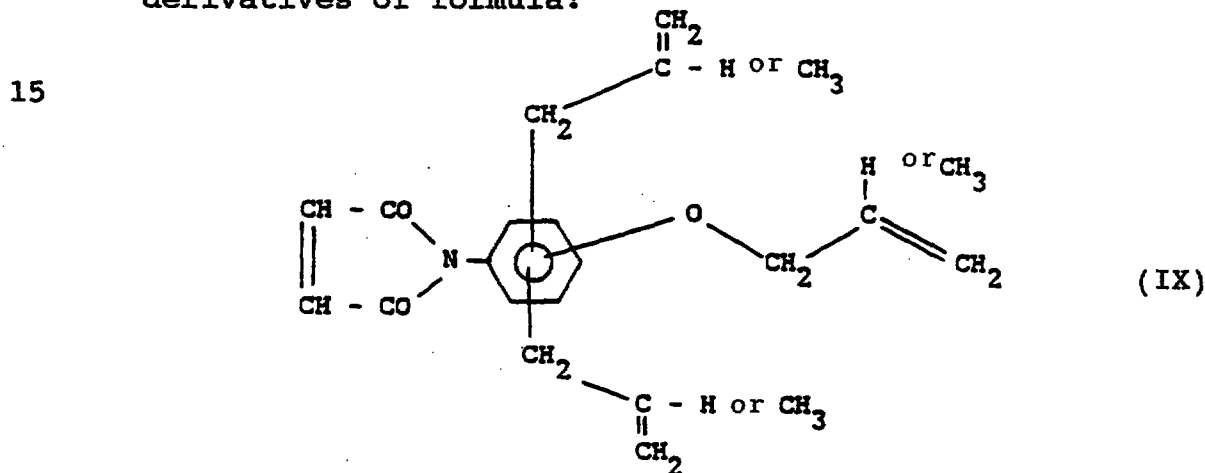
in which the allyloxy or methallyloxy radical is in the ortho, meta or para position with respect to the carbon atom of the benzene ring linked to the nitrogen;

- with:

10 • at least one monosubstituted derivative of formula:



• and optionally one or more disubstituted derivatives of formula:



In the abovementioned compound serving as a reactant (d₂), the proportions of the various constituents of the mixture of the products of formulae (VII), (VIII) and optional (IX) may vary within wide limits. In general, the proportions of the constituents are chosen to be between the following limits (expressing the percentage by weight of each of the constituents in the mixture):

20
25 - at least 30%, and preferably from 50% to 80%, of N-(meth)-allyloxyphenylmaleimide of formula (VII),

- from 5% to 50%, and preferably from 10% to 35%, of mono(meth)allyl substituted derivatives(s) of formula (VIII),

5 - and from 0% to 20%, and preferably from 0% to 15%, of di(meth)allyl substituted derivative(s) of formula (IX), the sum of the constituents having in each case to be equal to 100% by weight.

*when it is desired, for example, to improve further the flexural properties in the heated state:

10 (d₃) one or more substituted heterocyclic compounds containing one or more carbon-carbon double bonds.

It should be clearly understood that mixtures of reactants (d₁)+(d₃) or (d₂)+(d₃) can be used as reactant (d).

15 As regards the optional reactant (d₁), this is chosen from:

N-(2-allyloxyphenyl)maleimide,
N-(3-allyloxyphenyl)maleimide,
N-(4-allyloxyphenyl)maleimide,
20 N-(2-methallyloxyphenyl)maleimide,
N-(3-methallyloxyphenyl)maleimide,
N-(4-methallyloxyphenyl)maleimide, and mixtures thereof.

The maleimides of formula (VII) are known products which are described in European Patent Application
25 EP-A1-0,208,634.

As regards the optional reactant (d₂), the crude product obtained by carrying out the process defined below is preferably used as a compound comprising a mixture of N-(meth)allyloxyphenylmaleimide of formula
30 (VII) with one or more (meth)allyl substitution derivatives of formula(e) (VIII) and optionally (IX)

This process is characterised in that it consists in carrying out the following 3 stages, which are performed sequentially in the same reactor:

35 the first stage consists in reacting an amino-phenol in a solvent medium with maleic anhydride, working at a temperature ranging from 20°C to 200°C, for a period ranging, according to the temperature selected, from 30 minutes to 2 hours, and it leads to a first reaction

medium comprising an N-(hydroxyphenyl)maleamic acid;

the second stage consists in carrying out a (meth)allylation reaction of the abovementioned acid, by reacting the abovementioned first reaction medium with a (meth)allyl halide, working at a pH which must be adjusted and maintained at a constant value between 7 and 14 by adding a specified quantity of an alkaline aqueous solution, and at a temperature ranging from 40°C to 150°C, and it leads, after acidification and removal of the aqueous phase, to a second organic reaction medium comprising an N-[(meth)allyloxyphenyl]maleamic acid, one or more N-[(meth)allyloxy, (meth)allylphenyl]maleamic acids and, where appropriate, one or more N-[(meth)allyloxy, di(meth)allylphenyl]maleamic acids;

the third stage consists in carrying out a cyclisation reaction of the abovementioned maleamic acids, by reacting the abovementioned second reaction medium with a lower carboxylic acid anhydride in the presence of a tertiary amine and optionally a catalyst, and then in removing the reaction solvent, and it leads to a crude reaction product which is a compound comprising a mixture composed of the following: at least 30% by weight, and preferably from 50% to 80%, of N-[(meth)allyloxyphenyl]maleimide from 5% to 50% by weight, and preferably from 10% to 35% by weight, of one or more N-[(meth)allyloxy, (meth)allylphenyl]maleimides and from 0% to 20% by weight, and preferably from 0% to 15% by weight, of one or more N-[(meth)allyloxy, di(meth)allylphenyl]maleimides.

The 3 stages which have just been described are performed sequentially in a single solvent in order to enhance the simplicity of the process, but it is possible to perform a change of solvent during any stage without any disadvantage being incurred. The choice of solvent can be very wide, but since the second stage is carried out in a two-phase aqueous-organic medium, it may be desirable to employ a water-immiscible organic solvent, thereby considerably simplifying the treatment of the reaction mass. Among water-miscible or -immiscible

solvents which are usable, preference will, in fact be given to those which dissolve the starting aminophenol under the temperature conditions adopted for the synthesis. Among these solvents, there may be mentioned, for example: alcohols (for example methanol, ethanol, butanol); ketones (for example acetone, methyl ethyl ketone, methyl isobutyl ketone); nitriles (for example benzonitrile, propionitrile, acetonitrile); esters (for example ethyl or butyl acetate); aromatic solvents (for example anisole, chlorobenzene); and halogenated hydrocarbons (for example chloroform, dichloromethane, dichloroethane).

As regards the first stage of the process, it may be pointed out that the concentration of the starting reactants in the solvent used is not critical. Nevertheless, no advantage is gained either by diluting the reactants excessively, in the interest of productivity, or by concentrating them excessively, in order that the mixture shall be readily stirrable. In this first stage, the maleic anhydride is used in quantities at least equal to one mole per mole of aminophenol; larger quantities, namely of the order of 1.01 to 1.5 moles per mole of aminophenol, are generally used. In addition, the temperature is preferably between 40°C and 60°C.

As regards the second stage, this is begun by adding to the reaction medium the quantity of an alkaline aqueous solution, for example an aqueous NaOH solution, required on the one hand for salifying the N-(hydroxyphenyl)maleamic acid, and on the other hand for obtaining the desired pH. The pH will be held constant throughout the reaction by adding sodium hydroxide; preferably, the pH is adjusted and held at a constant value between 10 and 12. The allylation reaction is preferably carried out with (meth)allyl bromide or chloride. The quantity of (meth)allyl halide is of the order of 1.5 to 10 moles per mole of phenolic OH group, and preferably of the order of 2 to 4. The excess of this reactant can be recovered at the end of the operation and recycled in a following operation. The time taken for adding the (meth)allyl

halide is not critical, and it can fall within the range from 1 hour to 5 hours, and preferably from 2 hours to 4 hours. In this second stage, the temperature is preferably between 60°C and 100°C. It should be noted that, at the end of the stage, the aqueous phase is acidified to a pH approximately equal to 1 with the usual acids, preferably inorganic hydracids or oxyacids. The aqueous layer is removed and the organic layer left in the reactor.

As regards the third stage of the process, acetic anhydride, in quantities at least equal to one mole per mole of HOOC-CH=CH-CO-NH- group to be cyclised, is advantageously used as a lower carboxylic acid anhydride. Larger quantities, namely of the order of 1.05 to 1.5 moles per maleamic group, are generally used.

Among suitable tertiary amines, there may be mentioned, in particular, trialkylamines as well as N,N-dialkylanilines in which the alkyl radicals have from 1 to 12 carbon atoms. Triethylamine and N,N-dimethylaniline are advantageously used. The quantities of tertiary amine are between 0.05 to 2 moles per mole of HOOC-CH=CH-CONH- group.

As catalysts, it is possible to use, for example, nickel salts of carboxylic acids, optionally hydrated, as well as the chelated forms of this metal. The acetate and acetylacetonate are especially suitable. These catalysts are employed in very small quantities, of the order of 0.05 to 1.5 g per mole of HOOC-CH=CH-CO-NH- group, and preferably of the order of 0.1 to 0.8 g.

In this third stage, the temperature is not critical and only influences the kinetics of the reaction. This temperature may be, for example, between 40°C and 150°C, and is preferably between 60°C and 80°C. At the end of this stage, the solvent is removed by vacuum distillation and the crude reaction product, having the appearance of an oil, is obtained.

According to a greatly preferred embodiment of the present invention, the abovementioned process is readily applied, starting with meta-aminophenol, to the

preparation of compounds comprising mixtures based on:
N-[3-(meth)allyloxyphenyl]maleimide + N-[3-(meth)allyl-
oxy-4-(meth)allylphenyl]maleimide + N-[3-(meth)allyloxy-
6-(meth)allylphenyl]maleimide +, where appropriate, N-[3-
5 (meth)allyloxy-4,6-di(meth)allylphenyl]maleimide.

It should be noted that, starting with ortho-aminophenol, compounds are produced comprising mixtures based on:

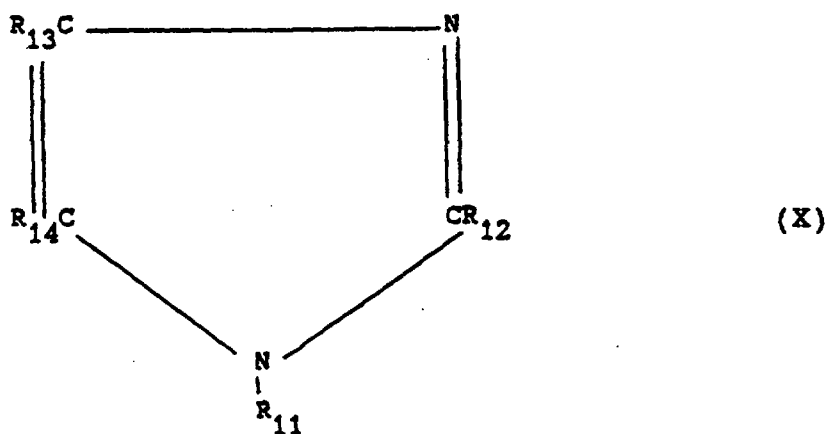
10 N-[2-(meth)allyloxyphenyl]maleimide + N-[2-(meth)allyl-
oxy-3-(meth)allylphenyl]maleimide + N-[2-(meth)allyloxy-
5-(meth)allylphenyl]maleimide +, where appropriate, N-[2-
(meth)allyloxy-3,5-di(meth)allylphenyl]maleimide.

It should also be noted that, starting with para-amino-
phenol, compounds are produced comprising mixtures based
15 on: N-[4-(meth)allyloxyphenyl]maleimide + N-[4-(meth)-
allyloxy-3-(meth)allylphenyl]maleimide +, where appro-
priate, N-[4-(meth)allyloxy-3,5-di(meth)allylphenyl]-
maleimide.

As regards the optional reactant (d_3), this is
20 chosen from vinylpyridines, N-vinylpyrrolidone, allyl
isocyanurate, triallyl isocyanurate and vinyltetra-
hydrofuran.

The reactivity of the constituents (a), (b), (c)
and, where appropriate (d) of the polymerisation medium
25 according to the invention may be increased, for example
when the applications envisaged require operations to be
carried out on an injection moulding machine, by adding
a catalyst (e) which can be either (e_1) a free-radical
polymerisation initiator such as, for example, dicumyl
30 peroxide, lauroyl peroxide or azobisisobutyronitrile, or
(e_2) an imidazole compound.

The said imidazole compound (e_2) corresponds to
the general formula:



in which R_{11} , R_{12} , R_{13} and R_{14} , which may be identical or different, each denote a hydrogen atom, an alkyl or alkoxy radical having from 1 to 20 carbon atoms, or a vinyl, phenyl or nitro radical, it being possible for R_{13} to form with R_{14} and the carbon atoms to which these radicals are bound a single ring such as, for example, a benzene ring, it also being possible for R_{11} to denote a carbonyl group bound to a second imidazole ring.

As specific examples of imidazole compounds (e_2), there may be mentioned, in particular: imidazole or glyoxaline, 1-methylimidazole, 2-vinylimidazole, 1,2,-dimethylimidazole, 1-vinylimidazole, 1-vinyl-2-methylimidazole, benzimidazole and carbonyldiimidazole.

In the heat-resistant polymers which have just been defined, the quantities of reactants (a) and (c) are chosen so as to have, by weight with respect to the total weight of these constituents:

from 50 to 98%, and preferably from 70 to 90%, of bis(maleimide)(s) (a) of formula (I), and

from 2 to 50%, and preferably from 10 to 30%, of diamine(s) (c) of formulae (III), (IV) and/or (V).

As regards the quantity of bis(maleimide)-siloxane (b) of formula (II), this generally represents less than 40%, and preferably from 5 to 30%, of the total weight of the reactants (a) + (c). Still more preferably, this quantity represents from 10 to 20% of the total weight of the reactants (a) + (c).

As regards the quantity of the optional reactant

(d), this generally represents less than 60%, and preferably from 5% to 50%, of the total weight of the reactants (a) + (c).

5 As regards the optional catalyst (e), according to its nature and according to the rate of polymerisation desired at the stage when the reaction is carried out, it is employed at a level falling within the range from 0.01 to 1% by weight with respect to the combination of the reactants (a) + (b) + (c) +, optionally, (d) and preferably
10 ably within the range from 0.05 to 0.5%.

The polymers according to the invention may be prepared by directly heating the reactant (a), the reactant (b), the reactant (c) and optionally the reactant (d) with, if required, the catalyst (e), at least
15 until a homogeneous liquid mixture is obtained. the temperature may vary according to the physical state of the compounds present, but is generally between 50°C and 300°C. It is advantageous to bring the starting compounds to, and maintain them in, a state of intimate mixture
20 before and during the heating, for example using efficient stirring. When the compound (e) is employed, the latter is preferably added at the beginning to the well stirred reaction mixture containing the reactants. When this compound is particularly active, in order to avoid
25 its encapsulation in the polymer network formed, it is desirable to add it in a solvent or diluent which is compatible with the reaction medium; it was found that it could be advantageous to use as solvent or diluent either the reactant (b), or alternatively one of the
30 polar organic liquids referred to below.

The preparation of the polymers according to the invention may also be accomplished by heating the mixture of reactants in an organic diluent which is liquid over at least part of the range 50°C-250°C. Among these
35 diluents, there may be mentioned, in particular, aromatic hydrocarbons such as xylenes and toluene, halogenated hydrocarbons such as chlorobenzenes, polar solvents such as dioxane, tetrahydrofuran and dibutyl ether, dimethylformamide, dimethyl sulphoxide, N-methylpyrrolidone,

dimethylacetamide, methyl glycol, cyclohexanone of (sic) methyl ethyl ketone. The solutions or suspensions of polymers may be employed as they are for many applications; it is also possible to isolate the polymers, for example by filtration, where appropriate after precipitation by means of an organic diluent which is miscible with the solvent employed. In this context, it is advantageously possible to use a hydrocarbon whose boiling point does not substantially exceed 120°C.

It should be understood that the properties of the polymers according to the invention may vary widely, depending in particular on the exact nature of the reactants introduced, the chosen proportions of reactants and the precise conditions of temperature adopted within the range stated above. As regards the polymers obtained, the latter may be cured polymers which are insoluble in the usual solvents such as, for example, the compounds mentioned in the preceding paragraph, and which do not show significant softening below the temperature at which they begin to decompose.

However, these polymers can also take the form of prepolymers (P) which are soluble in polar organic solvents and possess a softening point at a temperature below 200°C (in general this softening point is between 50° and 150°C). These prepolymers may be obtained in bulk by heating the mixture of reactants until a homogeneous or pasty product is obtained, at a temperature generally between 50° and 180°C, for a period which can range from a few minutes to a few hours, this period becoming shorter as the temperature adopted is raised. Before the mixture of reactants is subjected to heating, it is advantageous, in this case also, to mix its constituents intimately beforehand by stirring. In this case also, there is a preferred method for introducing the compound (e), this being the method described above in relation to the direct preparation of cured polymers. The preparation of the prepolymers may also be performed in suspension or in solution in a diluent which is liquid over at least part of the range 50° - 180°C.

It should be noted that these prepolymers (P) can also be obtained by forming, from the reactants (a) and (c), a prepolymer (PP) which is then reacted with the reactant (b) and, if required, the compounds (d) and/or (e). It is also possible to prepare beforehand a prepolymer (P'P') by heating the mixture of the reactants (b) and (c) and then reacting it with the reactant (a) and, if required, the compounds (d) and/or (e) to obtain the prepolymer (P). The conditions of temperature and time used for the preparation of the prepolymers (PP) or (P'P') and for their conversion to prepolymers (P) are those described above in relation to the preparation of the prepolymers (P) by directly mixing the reactants (a), (b), (c) and optionally (d) with, if required, the compound (e).

The prepolymers (P) may be used in the bulk liquid state, simple hot casting sufficing for shaping and producing moulded articles. It is also possible, after cooling and grinding, to use them in the form of powders which are exceptionally suitable for compression moulding operations, optionally in the presence of fillers in the state of powders, spheres, granules, fibres or flakes. In the form of suspensions or solutions, the prepolymers (P) may be used for producing coatings and preimpregnated intermediate articles whose reinforcement may consist of fibrous materials based on aluminium silicate or oxide or zirconium silicate or oxide, carbon, graphite, boron, asbestos or glass. It is also possible to use these prepolymers (P) for producing cellular materials after the incorporation of a blowing agent such as, for example, azodicarbonamide.

In a second stage, the prepolymers (P) may be cured by heating to temperatures of the order of 300°C, generally between 150°C and 250°C; an additional shaping may be performed during the curing, optionally under vacuum or under pressure above atmospheric pressure, it also being possible for these operations to be consecutive.

It does not constitute a departure from the scope

of the invention if polymers according to the invention, which are not in the form of prepolymers (P), are prepared using an intimate mixture of prepolymer (PP), reactant (b) and, if required, compounds (d) and/or (e),
5 or an intimate mixture of prepolymer (P'P'), the reactant (a) and, if required, compounds (d) and/or (e), which is heated in bulk under the conditions described above.

The polymers according to the invention are of value in industrial fields requiring materials endowed
10 with good mechanical and electrical properties as well as great chemical inertness at temperatures of 200°C to 300°C. By way of examples, they are suitable for the manufacture of insulators in plate or tubular form for electrical transformers, printed circuit bases, pinions,
15 rings, and the like. The preimpregnated articles are usable for the production of parts having a variety of shapes and functions in many industries such as, for example, in the aeronautical industry. These parts, referred to as laminates, which may be bodies produced by
20 rotation, are obtaining by depositing several layers of prepregs on a former or support. The prepregs can also be used as reinforcements or as a means of repairing damaged parts. It is also possible to contrive parts according to filament winding techniques, with or without a sup-
25 port; it is possible, as well, to carry out injection moulding or pultrusion. It will be recalled that, in order to make, for example, moulded articles, it is possible to use either the mixture of the reactants or a prepolymer (P) as the starting material. When the mixture
30 of the reactants is used directly as the starting material, this mixture is given the shape of the desired article and the curing is then performed by heating. When the prepolymer (P) is used as the starting material, it may be moulded by simple hot casting or by injection, and
35 its curing is then induced by heating.

The examples which follow are given by way of illustration but without implied limitation.

EXAMPLE 1

1. Example of implementation of the present invention:

The following are introduced at room temperature into a glass reactor equipped with an anchor type stirrer and a side tube permitting the escape of volatile products:

100 g (0.279 mole) of N,N'-(4,4'-diphenylmethane)-bis(maleimide), and

22 g (0.111 mole) of 4,4'-diaminodiphenylmethane.

The reaction mixture is brought with stirring to a temperature of 170°C for 5 minutes, and is then rapidly cooled to 140°C.

When this temperature has been reached, the mixture is outgassed, and 22 g (0.019 mole) of the bis(maleimide) containing a diorganopolysiloxane group which is described in section 2 below are then introduced with stirring.

The reaction mixture is then poured into a mould preheated to 150°C, for the purpose of preparing plates having the dimensions 140 x 100 x 4 mm, which will be subjected, in a ventilated oven, to the following curing cycle:

100 minutes between 150°C and 250°C (rate of temperature rise of the order of 1°C/minute),

16 hours at 250°C, and

2 hours at between 250°C and 25°C (rate of cooling of the order of 2°C/minute).

After release from the mould, the plates based on cured polymer are cut up in order to obtain test pieces:

having the dimensions 30 x 7 x 4 mm, on which the flexural breaking strength (Sf) and the flexural modulus (Mf) are measured (according to Standard ASTM D 790-71);

having the dimensions 60 x 10 x 4 mm, on which unnotched CHARPY impact tests are carried out at 25°C for measuring the surface resilience (Rc) (according to Standard NFT 51035);

having the dimensions 50 x 10 x 4 mm, on which the glass transition temperature (Tg) is measured by DMA

(Dynamic Mechanical Analysis). The Tg values are determined from the curves for flexural modulus as a function of temperature, obtained by dynamic mechanical analysis carried out on an apparatus referred to as DMA 983 of the company DU PONT. The temperature range explored extends from 25°C to 400°C, with a rate of temperature rise of 3°C/minute under an inert atmosphere. The resonance frequency is 20 Hz. The data are collected and processed by the apparatus referred to as a DU PONT 1090 Analyser.

By way of a comparative trial, the operations described above were repeated, but using the following reactants:

100 g (0.279 mole) of N,N'-(4,4'-diphenylmethane)-bis(maleimide), and

22 g (0.111 mole) of 4,4'-diaminodiphenylmethane.

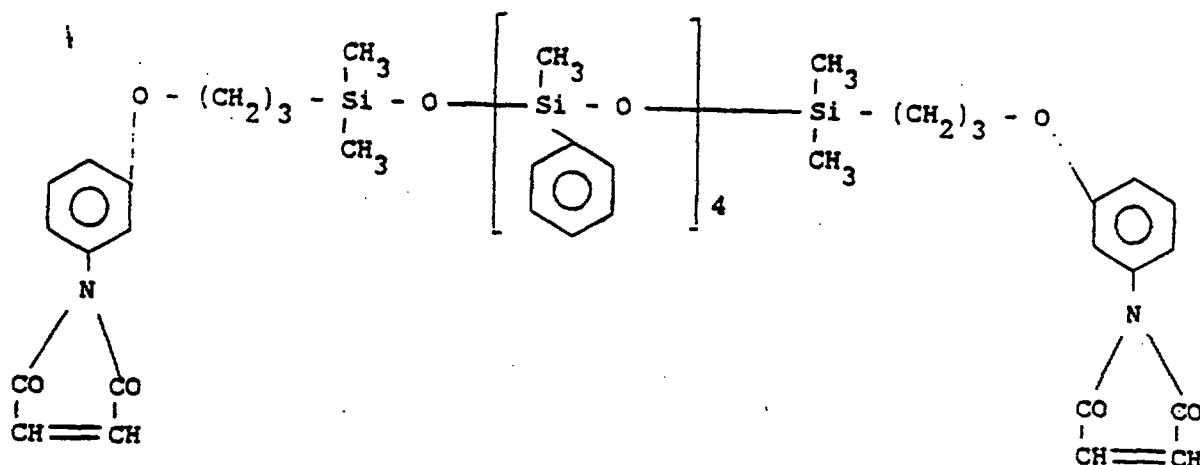
The reactants are introduced in the course of 4 minutes into the reactor preheated to 160°C. The mixture is then outgassed for 1 minute, and thereafter left to react at 160°C for a further 9 minutes.

The values for the mechanical properties are collated in the following table:

	Initial Sf		Initial Mf		Initial Rc	Tg in °C
	in MPa		in MPa		in kJ/m ²	
	at 25°C	at 250°C	at 25°C	at 250°C	at 25°C	
Ex1	98	50	2550	1300	9	260
Trial	226	93.2	3400	1500	5	300

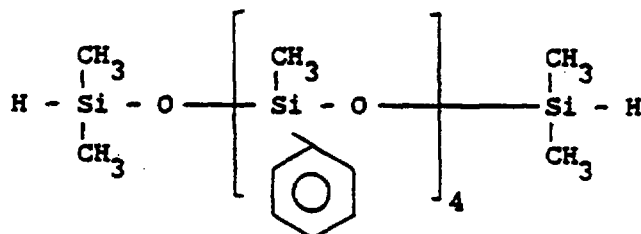
2. Description of the process for preparing the bis(maleimide) containing a diorganopolysilxane group used in Example 1:

This bis(maleimide) has the following formula:



2.1 Preparation of the diamine containing a diorganopolysiloxane group from which this bis(maleimide) is derived:

A glass reactor equipped with a central stirrer, a dropping funnel and a reflux condenser, in which a slight overpressure of dry nitrogen is established, is charged with 312 g (0.46 mole) of an alpha,omega-bis-(hydrogeno)diorganopolysiloxane of formula:

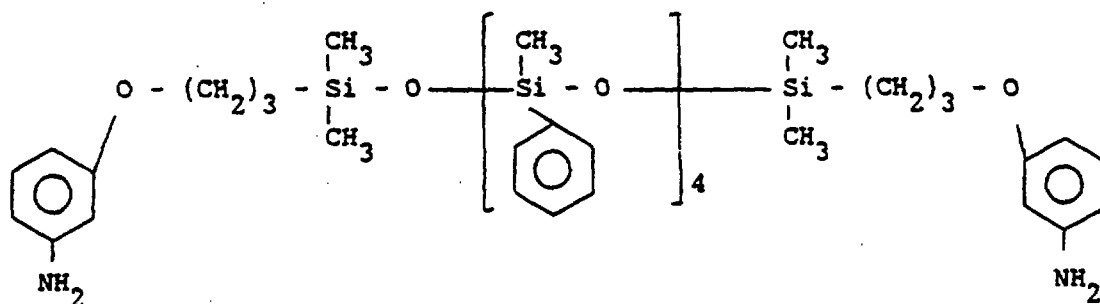


having a molecular mass of the order of 678 g.

The reactor is then placed in an oil bath pre-heated to 55°C, after which the catalyst is added. The latter is the Karstedt catalyst (complex based on elementary platinum and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane ligands): it is dissolved in toluene (concentration 3.5% by weight) and 1.49 cm³ of this catalyst solution are introduced with a syringe, the ratio r (weight of elementary platinum introduced/weight of the reaction mass) is equal to 91 x 10⁻⁶.

137 g (0.92 mole) of meta-allyloxylaniline are then allowed to flow gradually into the reactor during a period of 60 minutes, in order to control the exothermic nature of the reaction. Thirty minutes after the addition is complete, the mixture is returned to room temperature. The product obtained, weighing 448.9 g, is a clear viscous oil, orange-brown in colour, possessing a proton

NMR spectrum in agreement with the following structure:



The molecular mass is of the order of 976 g. Under these conditions, the degree of conversion of the reactants introduced is 100% (neither amine nor hydrogenated siloxane oligomer is detected by NMR and infrared analysis), and the yield by weight of desired diamine is 100%.

2.2 Preparation of the bis(maleimide)-diorganopolysiloxane:

The following are introduced simultaneously in the course of 10 minutes, using 2 dropping funnels, into a glass reactor equipped with a central stirrer and a reflux condenser, in which a slight overpressure of dry nitrogen is established and which is placed in an oil bath preheated to 55°C:

20 cm³ of a solution in acetone of 25 g (0.025 mole and 0.02 NH₂ group) of the siloxane-diamine prepared above in section 2.1, and

15 cm³ of a solution in acetone of 6.4 g (0.055 mole) of maleic anhydride.

When the additions are complete, each funnel is rinsed with 5 cm³ of acetone, which are then added to the reaction mass maintained with stirring for 15 minutes.

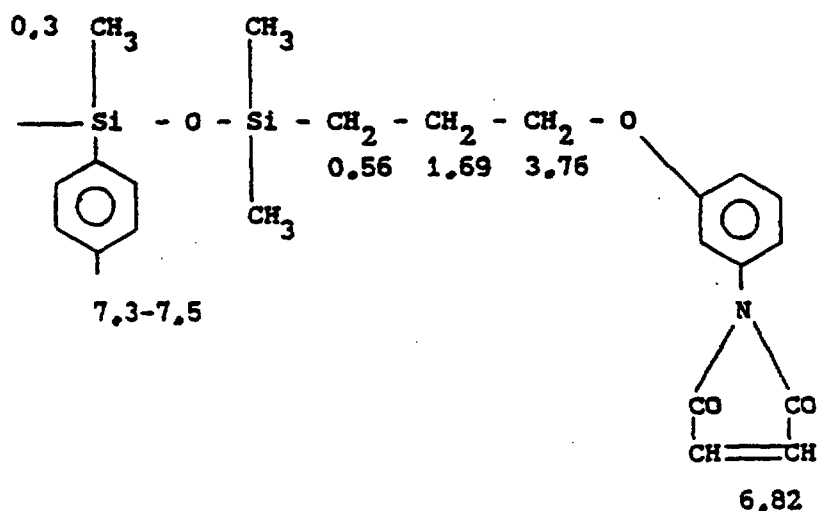
The dropping funnel which contained maleic anhydride is changed with 6.1 g (0.06 mole) of acetic anhydride, and the other funnel is charged with 1.67 g (0.0165 mole) of triethylamine.

These two compounds are then allowed to flow into the reactor, after which 0.3 cm³ of an aqueous solution

containing 0.0528 mole of nickel acetate for 100 cm³ of solution is added.

The reaction mixture is maintained under reflux with stirring for 2 hours 30 minutes. The temperature is then lowered to 20°C.

The reaction mixture is diluted with 80 cm³ of ice-cold water (5°C) with vigorous stirring, and the oily product present is then extracted with 80 cm³ of ethyl acetate. The organic phase obtained is washed with three times 80 cm³ of water so that a pH of 6 is obtained in the washing water, and then dried for 2 hours over anhydrous sodium sulphate. After filtration, the ethyl acetate is removed from the organic phase by evaporation, completing this operation under reduced pressure (approximately 70 Pa) at 60°C, and 27.3 g (equivalent to a yield of 96% by weight with respect to the theoretical value) of an orange-brown viscous product is collected, the NMR spectrum of which is in agreement with the structure of the desired bis(maleimide) which has been defined above. The molecular mass is of the order of 1136 g (sic). In proton NMR (solvent: CDCl₃; reference: tetramethylsilane), the absence of the starting diamine is noted and the following chemical shifts, expressed in ppm, are noted:



the ratio: number of Si-phenyl bonds
number of Si-methyl bonds

is found to be equal to 0.5.

In infrared spectrometry, the presence of the following bands is noted: ν (imide C=O) = 1710 - 1730 cm⁻¹;

ν (maleimide C-N-C) = 1160 cm^{-1} ; ν (C-N-C) = 1400 cm^{-1} .

EXAMPLE 2

The following are introduced at room temperature into the reactor used in Example 1:

5 100 g (0.279 mole) of N,N'-(4,4'-diphenylmethane)-bis(maleimide), and

 22 g (0.078 mole) of 4,4'-diamino-3,3'-diethyl-5,5'-dimethyldiphenylmethane.

10 The mixture is melted by bringing it to 170°C with stirring for 10 minutes, and it is then outgassed and cooled to 140°C. 22 g (0.019 mole) of the bis(maleimide) containing a diorganopolysiloxane group which is described in Example 1, mixed with 0.18 g of imidazole, are then introduced with stirring.

15 The reaction mixture is then moulded, cured and tested as described above in Example 1.

 The values for the mechanical properties are as follows:

 Results for flexural properties:

20 at 25°C: initial Sf = 103 MPa
 initial Mf = 2900 MPa (after ageing
 for 1000 hours at 250°C,
 this value remains
 unchanged).

25 at 250°C: initial Sf = 40 MPa
 initial Mf = 1500 MPa

 Surface resilience:

30 at 25°C: initial Rc = 10 kJ/m^2 (after ageing
 for 1000 hours at 250°C,
 this value falls to
 5 kJ/m^2).

Tg by DMA = 290°C.

35 Furthermore, the gel time of the prepolymer according to this example was measured. It is measured on a mixture of 10 g of the starting reactants using a SUNSHINE apparatus: zero time is defined by the instant of immersion of the tube containing the said mixture in a thermostated bath at the temperature of measurement: the gel time at 160°C is found to be equal to 19 minutes.

EXAMPLE 3

The following are introduced at room temperature into the reactor used in Example 1:

100 g (0.279 mole) of N,N'-(4,4'-diphenylmethane)-bis(maleimide), and

22 g (0.078 mole) of 4,4'-diamino-3,3'-diethyl-5,5'-dimethyldiphenylmethane.

The reaction mass is melted by bringing it to 170°C with stirring for 10 minutes, and is then outgassed and cooled to 140°C. A mixture consisting of 22 g (0.019 mole) of the bis(maleimide) containing a diorganopolysiloxane group which is described above in Example 1 and 10 g (0.090 mole) of N-vinyl-2-pyrrolidone is then added with stirring.

The gel time of the prepolymer according to this example is 15 minutes.

The reaction mass is then moulded, cured and tested as described above in Example 1.

The values for the mechanical properties are as follows:

Results for flexural properties:

at 25°C: initial Sf = 110 MPa

initial Mf = 3000 MPa (after ageing for 1000 hours at 250°C, this value remains unchanged).

at 250°C: initial Sf = 55 MPa

initial Mf = 1600 MPa

Surface resilience:

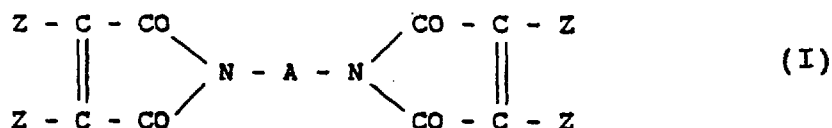
at 25°C: initial Rc = 11 kJ/m² (after ageing for 1000 hours at 250°C, this value falls to 5.5 kJ/m²).

Tg by DMA = 280°C.

CLAIMS

1. Polymers containing imide groups, characterised in that they comprise the product of reaction, at a temperature ranging from 50°C to 300°C, between:

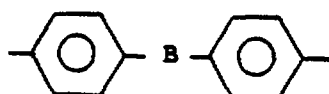
- 5 (a) 50 to 98% with respect to the total weight of the reactants (a) + (c) of an N,N'-bis(maleimide) or of a combination of several bis(maleimides) of formula:



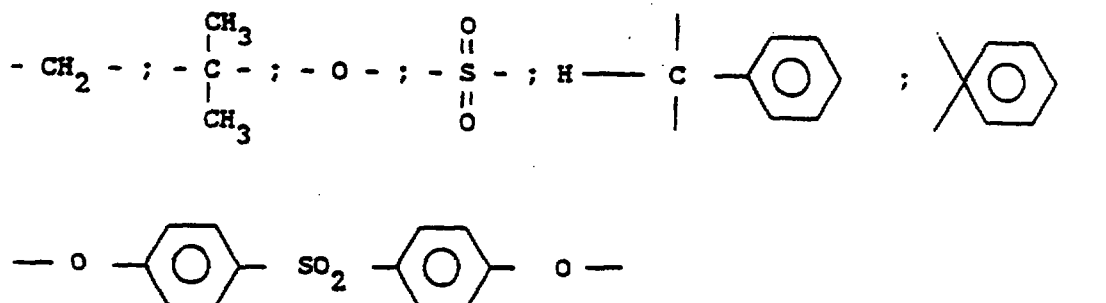
in which:

- 10 the symbols Z, which may be identical or different, each denote H, CH₃, or Cl;

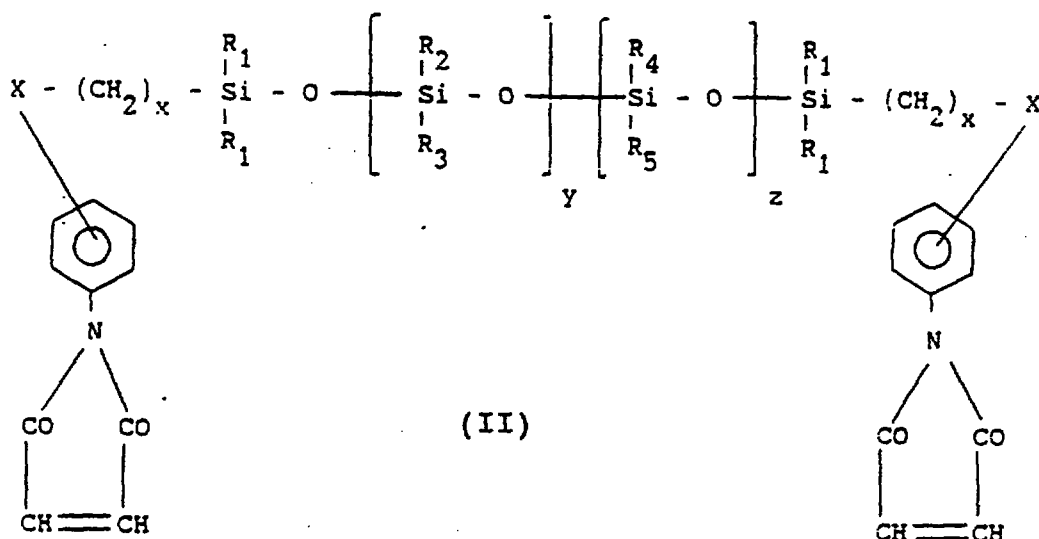
- the symbol A denotes a divalent radical chosen from the group consisting of the following radicals: cyclohexylenes; phenylenes; 4-methyl-1,3-phenylenes (sic); 2-methyl-1,3-phenylene; 5-methyl-1,3-phenylene; 2,5-diethyl-3-methyl-1,4-phenylene; and the radicals of formula:



in which B denotes a single valency bond or a group:

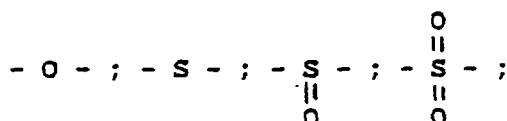


- 20 (b) at least 5% and less than 40% of the total weight of the reactants (a) + (c) of an N,N'-bis(maleimide) containing a diorganopolysiloxane group corresponding essentially to the general formula:



in which:

5 X, which is in the ortho, meta or para position with respect to the carbon atom of the benzene ring linked to the nitrogen denotes one of the following atoms or groups:



10 R₁, R₂, R₃, R₄ and R₅, which may be identical or different, each denote a monovalent hydrocarbon radical chosen from: linear or branched alkyl radicals having from 1 to 12 carbon atoms, it being possible for these radicals to be substituted with one or more chlorine, bromine or fluorine atoms or with a -CN group; a phenyl radical optionally substituted with one or more alkyl and/or alkoxy radicals having from 1 to 4 carbon atoms or
15 with one or more chlorine atoms;

the symbol X (sic) is an integer falling within the range from 2 to 8;

20 the symbols y and z denote numbers, which may be identical or different, integral or fractional, whose sum falls within the range from 0 to 100;



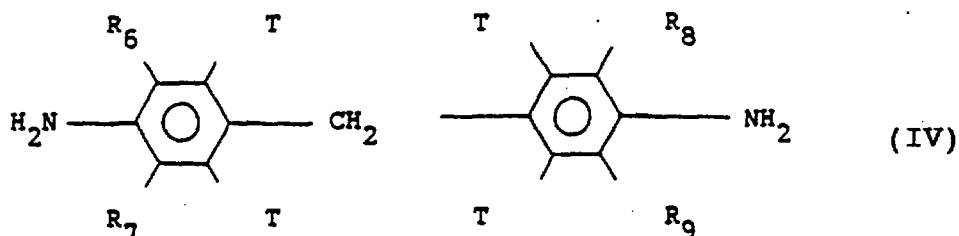
(c) 2 to 50% with respect to the total weight of the reactants (a) + (c) of one or more diprimary diamines selected from the group composed of:

5 *(c1) the species corresponding to the general formula:



10 in which the symbol E denotes one of the divalent radicals denoted by the symbol A of the formula (I), it being possible for the symbols A and E present in the same polymer to be identical to or different from one another;

*(c2) the species corresponding to the general formula:

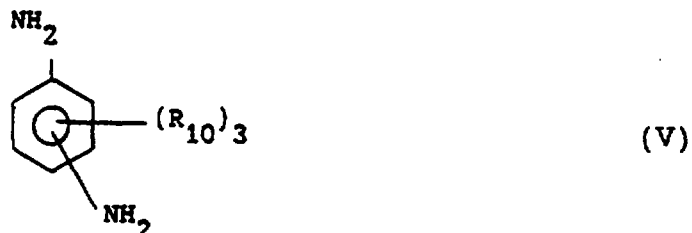


15 in which:

the symbols R_6 , R_7 , R_8 and R_9 , which may be identical or different, each denote a methyl, ethyl, propyl or isopropyl radical;

20 the symbols T, which may be identical or different, each denote a hydrogen atom or a chlorine atom; and

*(c3) the species corresponding to the general formula:



25 in which:

the amino radicals are in the meta or para position with respect to one another;

the symbols R_{10} , which may be identical or different, each denote a methyl, ethyl, propyl or



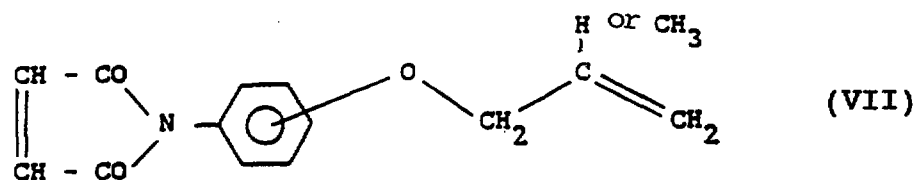
isopropyl radical;

(d) optionally, one or more monomers other than a bis(maleimide) of formula (I) or of formula (II) and containing one or more polymerisable carbon-carbon double bonds; and

(e) optionally, a catalyst.

2. Polymers according to claim 1, characterised in that the optional reactant (d), when one is used, consists of the following species:

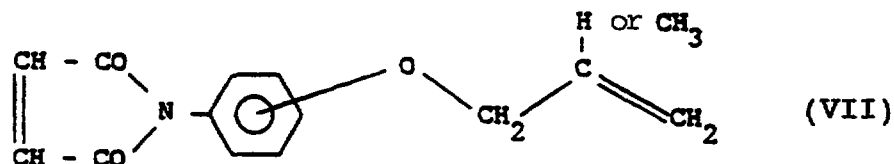
(d₁) either one or more monomers of formula:



in which the allyloxy or methallyloxy radical is in the ortho, meta (sic) or para position with respect to the carbon atom of the benzene ring linked to the nitrogen;

(d₂) or a compound comprising:

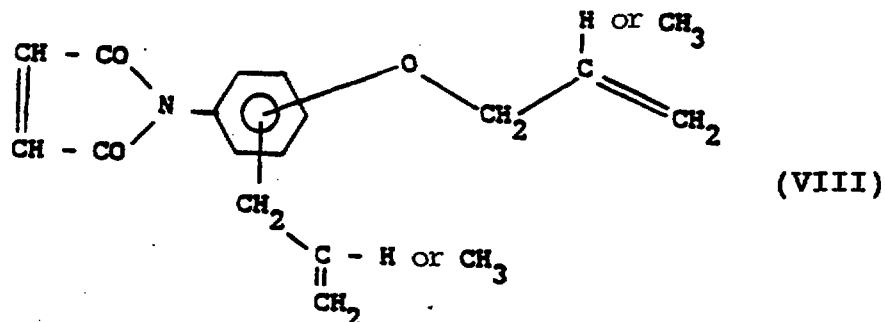
- a mixture of a monomer of formula:



in which the allyloxy or methallyloxy radical is in the ortho, meta or para position with respect to the carbon atom of the benzene ring linked to the nitrogen;

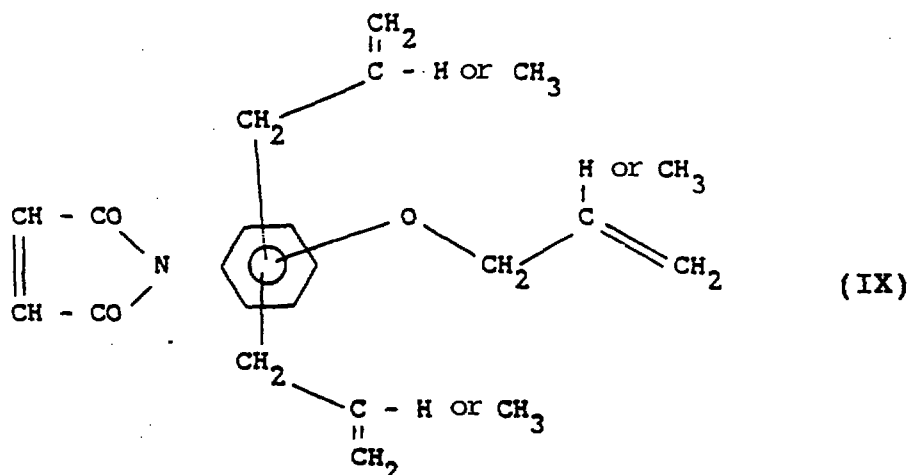
- with:

• at least one monosubstituted derivative of formula:



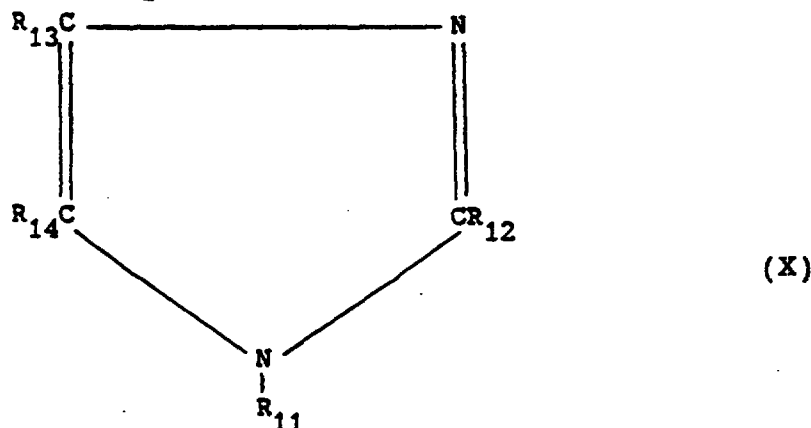


and optionally one or more disubstituted derivatives of formula:



5 (d₃) or one or more substituted heterocyclic compounds containing one or more carbon-carbon double bonds.

3. Polymers according to either of claims 1 and 2, characterised in that the catalyst (e), when one is used, is either (e₁) a free-radical polymerisation initiator, or
10 (e₂) an imidazole compound of formula:



15 in which R₁₁, R₁₂, R₁₃ and R₁₄, which may be identical or different, each denote a hydrogen atom, an alkyl or alkoxy radical having from 1 to 20 carbon atoms, or a vinyl, phenyl or nitro radical, it being possible for R₁₃ to form with R₁₄ and the carbon atoms to which these radicals are bound a single ring such as, for example, a benzene ring, it also being possible for R₁₁ to denote a carbonyl group bound to a second imidazole ring.

20 4. Polymers according to any one of claims 1 to 3, characterised in that:



* on the one hand: the quantities of reactants (a) and (c) are chosen so as to have, by weight with respect to the total weight of these constituents:

5 from 70 to 90% of the bis(maleimide)(s) (a) of formula (I), and

from 10 to 30% of diamine(s) (c) of formula (III), (IV) and/or (V);

10 * and on the other hand: as regards the quantity of bis(maleimide)-siloxane (b) of formula (II), this represents from 5 to 30% of the total weight of the reactants (a) + (c).

15 5. Polymers according to any one of claims 1 to 4, characterised in that the quantity of the optional reactant (d), when one is used, represents less than 60%, and preferably from 5% to 50%, of the total weight of the reactants (a) + (c).

20 6. Polymers according to any one of claims 1 to 5, characterised in that the optional catalyst (e), when one is used, is employed at a level falling within the range from 0.01 to 1%, and preferably from 0.05 to 0.5%, by weight with respect to the combination of the reactant (sic) (a) + (b) + (c) +, optionally, (d).

25 7. Polymers according to any one of claims 1 to 6, characterised in that they take the form of cured polymers which are insoluble in the usual solvents and which do not show significant softening below the temperature at which they begin to decompose.

30 8. Polymers according to any one of claims 1 to 6, characterised in that they take the form of thermosetting prepolymers (P) which are soluble in polar organic solvents and possess a softening point at a temperature below 200°C.

35 9. Process for preparing cured polymers according to claims 1 to 7, characterised in that the mixture of the reactants is heated directly to a temperature of between 50°C and 300°C, working in bulk or in an organic diluent.

10. Preparation process according to claim 9, characterised in that it consists in heating the mixture of the reactants to between 50°C and 180°C to form, in a first



stage, a prepolymer (P), and then inducing the curing of the prepolymer (P) by heating to a temperature of between 150°C and 250°C.

5 11. Process for preparing thermosetting polymers (P) according to claims 1 to 6 and 8, characterised in that the mixture of the reactants is heated directly to a temperature of between 50°C and 180°C, working in bulk or in an organic diluent.

10 12. Preparation process according to any one of claims 9 to 11, characterised in that, when the reaction is performed in bulk, the bis(maleimides) of formula (II) in which the ratio:

15
$$\frac{\text{number of Si-phenyl (optionally substituted) bonds}}{\text{number of Si-alkyl bonds}}$$

is equal to at least 0.25 are used as reactant (b).

20 13. Application of the prepolymers according to any one of claims 1 to 8 to the manufacture of moulded articles, coatings, articles having a cellular structure and reinforced and impregnated composite materials.