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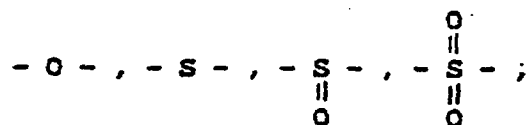
[illegible]

(I)

in which:

- X, which is in an ortho, meta or para position relative to the nitrogen-bonded carbon atom of the benzene ring, denotes an atom or group which follows:

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10 - each of R_1, R_2, R_3, R_4 and R_5 , which are identical or different, denotes a monovalent hydrocarbon radical chosen from: linear or branched alkyl radicals containing from 1 to 12 carbon atoms, it being possible for these radicals to be substituted by one or more chlorine, bromine or fluorine atoms or by a -CN group; a phenyl radical substituted, if desired, by one or more alkyl and/or alkoxy radicals containing from 1 to 4 carbon atoms or by one or more chlorine atoms,

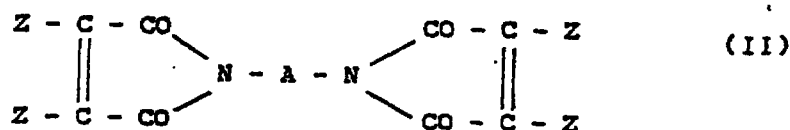
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- the symbol x is an integer situated in the range from 2 to 8,

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- the symbols y and z denote identical or different, whole or fractional numbers whose sum is situated in the range from 0 to 100;

- (b) an N,N'-bismaleimide or a combination of a number of bismaleimides of formula:



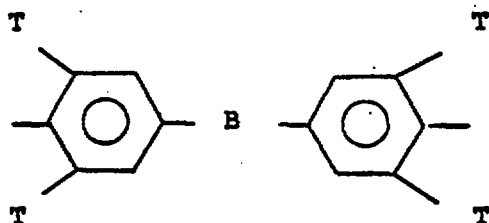
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in which:

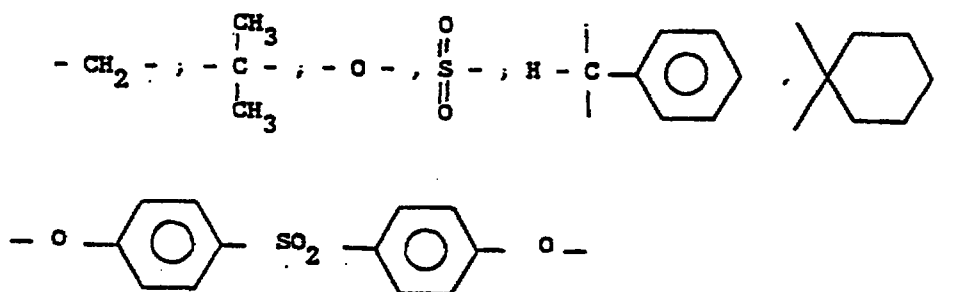
- each of the symbols Z, which are identical or different, denotes H, CH_3 , or Cl,

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- the symbol A denotes a divalent radical chosen from the group consisting of the cyclohexylene, phenylene, 4-methyl-1,3-phenylene, 2-methyl-1,3-phenylene and 5-methyl-1,3-phenylene and 2,5-diethyl-3-methyl-1,4-phenylene radicals, and the radicals of formula:



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



and each of the symbols T, which are identical or different, denotes a hydrogen atom or a methyl, ethyl or isopropyl radical;

- (c) if desired, one or more monomers other than a bismaleimide of formula (I) or of formula (II) and containing one or more polymerisable carbon-carbon double bonds; and

- (d) a catalyst, if desired.

On the subject of the bismaleimides of formula (I), when y and/or z are greater than 1 the compound present is polymeric in structure and is rarely a single compound, but is in most cases a mixture of compounds of the same chemical structure, which differ in the number of repeat units in their molecule; this leads to a mean value of y and/or z which may be whole or fractional.

When the preparation of the polymers according to the invention is carried out, according to the directions given hereinafter, in an organic diluent or solvent, any one of the compounds of formula (I) may be employed.

As bismaleimides which are preferentially

representative, there may be mentioned those which correspond to the formula (1) in which:

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

As bismaleimides which are even more preferentially representative, there may be mentioned those which correspond to the formula (I) in which:

5. $X = -O-$; $R_1 = R_2 = R_3 = R_4 = R_5 =$ linear alkyl radical containing from 1 to 3 carbon atoms; $x = 2, 3$ or 4 ; $y + z$ is situated in the range from 0 to 100, and preferably from 4 to 70.
6. $X = -O-$; $R_1 = R_2 = R_3 =$ linear alkyl radical containing from 1 to 3 carbon atoms; $R_4 = R_5 \dots$ [sic] phenyl radical;
 $x = 2, 3$ or 4 ; $y + z$ is situated in the range from 0 to 100, and preferably from 4 to 70.
7. $X = -O-$; $R_1 = R_2 = R_4 =$ linear alkyl radical containing from 1 to 3 carbon atoms; $R_3 = R_5 =$ a phenyl radical;
 $x = 2, 3$ or 4 ; $y + z$ is situated in the range from 0 to 100, and preferably from 4 to 70.

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

5 As bismaleimides which are very particularly representative, there may be mentioned those which correspond to formula (I) in which:

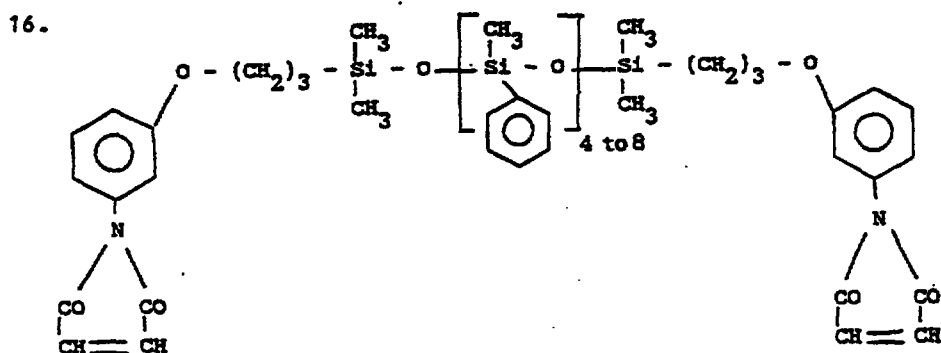
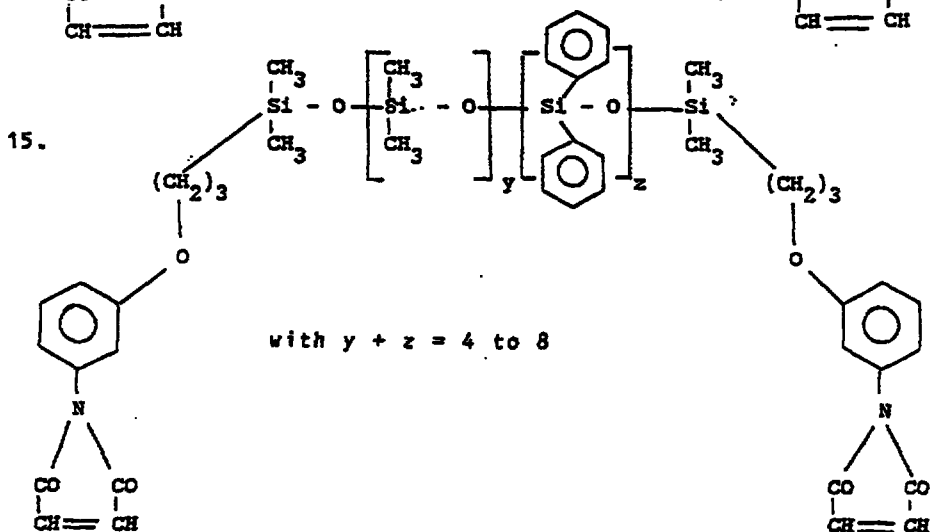
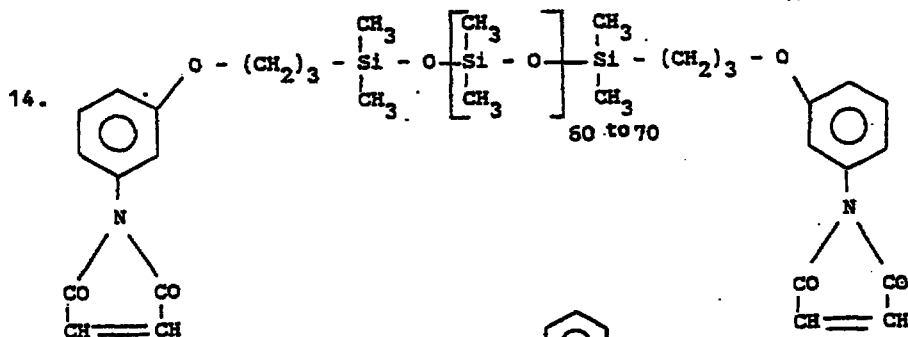
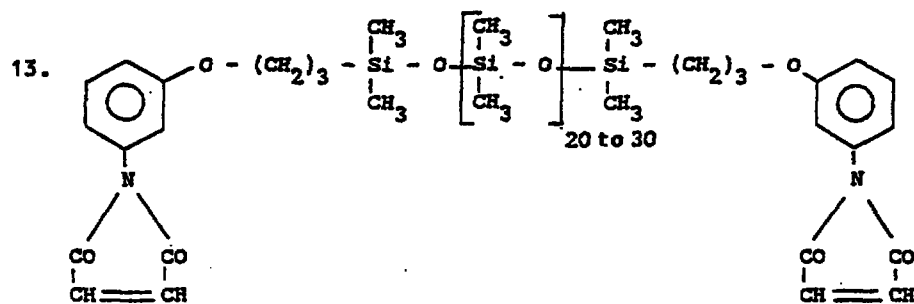
9. $X = -O-$; $R_1 = R_2 = R_3 = R_4 = R_5$ = methyl radical; $x = 3$; $y + z$ is situated in the range from 0 to 100, and preferably from 4 to 70.

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

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

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

20 As specific examples of bismaleimides which are very particularly representative, there may be mentioned in particular:



When the preparation of the polymers according to the invention is carried out in bulk, the bismaleimides of formula (I) which are preferably employed are those in

which the diorganopolysiloxane group contains a plurality of Si-phenyl or Si-substituted phenyl bonds. Bismaleimides of this type which are suitable are those belonging to the following groups, classified in an increasing order of preference:

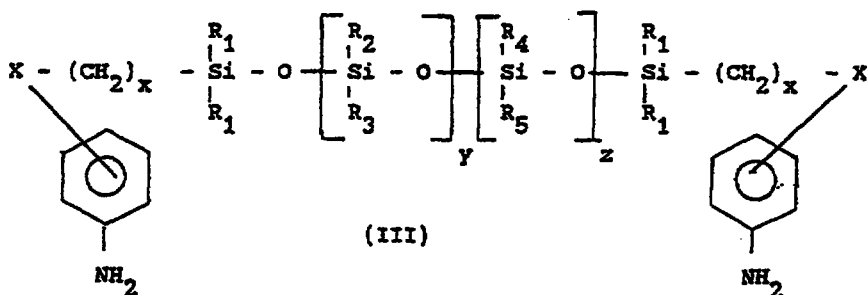
- bismaleimides no. 2, 3 and 4;
- bismaleimides no. 6, 7 and 8;
- bismaleimides no. 10, 11 and 12.

Among the bismaleimides belonging to these preferred groups, those which are very particularly suitable for preparing polymers in bulk are the compounds in which the ratio:

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

is at least equal to 0.25; by way of specific examples of bismaleimides of this type, reference will be made particularly to the compounds [sic] no. 16.

The bismaleimides of formula (I) are original 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:

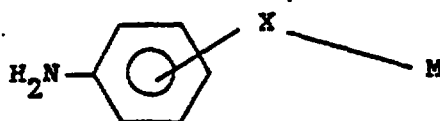


in which X, R₁, R₂, R₃, R₄, R₅, x, y and z have the meanings given above for formula (I).

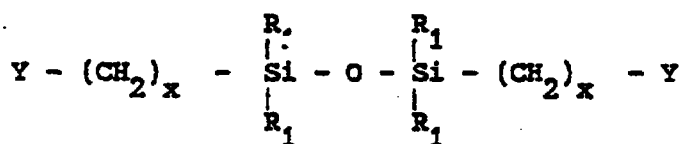
These diamines (III) containing a diorganopolysiloxane group are compounds which are well known in the prior art. They are described, for example, in British Patent GB-B-1,062,418 and in US Patent US-A-4,395,527.

According to these documents, a first method for the preparation of these diamines, which is applicable

especially when it is possible to obtain a compound of formula (III) where $y = z = 0$, that is to say when it is possible to obtain a diamine containing a diorganodisiloxane group, consists in reacting a compound of formula

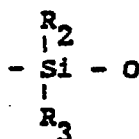


where X has the meaning given above and M is an alkali or alkaline-earth metal, with a bis(haloalkyl)disiloxane of formula:

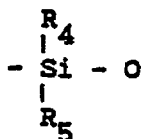


where x has the value shown above and Y is a chlorine, bromine or iodine atom, by operating at a temperature of between 20° and 200°C in the presence of an aprotic polar solvent.

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



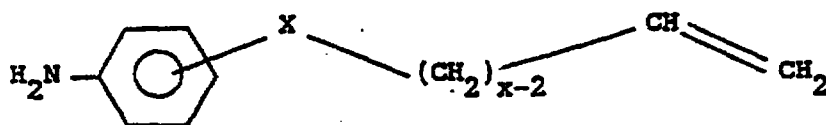
and/or z moles of siloxy groups of formula:



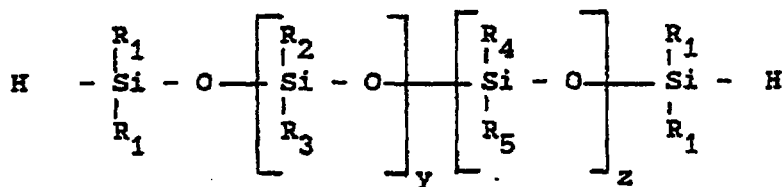
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In general, the reaction takes place at a temperature of between 80° and 250°C in the presence, again, of a solvent and, if desired, of a suitable catalyst.

Another way of preparing the diamines of formula (III), with y and/or z being equal to zero or other than zero, is to react a compound containing ethylenic unsaturation of formula:



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



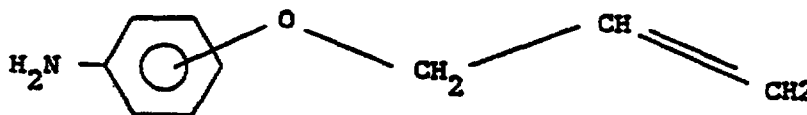
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in which R₁, R₂, R₃, R₄, R₅, y and z have the meanings given above. This hydrosilylation reaction is carried out by operating in bulk in the absence of solvent and by employing a platinum-based catalyst. The alpha, omega-bis(hydro)diorganopolysiloxanes employed are products which are well known in the silicone industry and which

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are, in some cases, available commercially. They are described, for example, in French Patents FR-A1-2,486,952 and FR-A5-2,058,988.

5 When it is decided to make use of this hydro-silylation reaction in order to prepare a diamine of formula (III), the amine substrate containing ethylenic unsaturation which is well adapted to react with the alpha, omegabis(hydro)diorganopolysiloxane consists particularly of an allyloxylaniline of formula:



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These privileged conditions, therefore, lead to diamines of formula (III) which will be used to manufacture some of the bismaleimides of formula (I), that is to say those where $\text{X} = -\text{O}-$, $x = 3$ and $\text{R}_1, \text{R}_2, \text{R}_3, \text{R}_4, \text{R}_5, \text{y}$ and z have the general or specific meanings given above.

To return to the process for the preparation of the bismaleimides of formula (I), the diamine of formula (III) is reacted, as indicated above, with maleic anhydride in the presence of a dehydrating agent, a tertiary amine, an organic diluent and a catalyst.

Maleic anhydride is employed in quantities which are at least equal to one mole per available NH_2 functional group; generally, larger quantities are employed, which are of the order of 1.01 to 1.5 moles per available NH_2 functional group.

The dehydrating agent employed is advantageously a lower carboxylic acid anhydride such as acetic anhydride in a quantity at least equal to one mole per available NH_2 functional group present in the molecule of the diamine of formula (III) which is employed. Generally, larger quantities are employed, which are of the order of 1.05 to 1.5 moles per available NH_2

functional group.

Among the tertiary amines which are suitable, there may be mentioned particularly made of trialkylamines and of N,N-dialkylanilines in which the alkyl radicals contain from 1 to 12 carbon atoms. Triethylamine and N,N-dimethylaniline are advantageous in use. The quantities of tertiary amines are generally situated between 0.05 and 0.8 moles per available NH_2 functional group.

The reaction is carried out in a liquid organic diluent under operating conditions in practice between 20° and 100° at atmospheric pressure. Among the solvents which may be employed preference will be given to those which dissolve the starting maleic anhydride in the temperature conditions chosen for the reaction and in the presence of the other constituents of the reaction mixture.

Among these, there may be mentioned particularly:

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

The catalysts which may be employed are a nickel derivative soluble in the liquid phase of the reaction mixture such as, for example, nickel salts of carboxylic acids, hydrated if desired, and the chelated forms of this metal. The acetate and the acetylacetonate are particularly suitable. These catalysts are employed in very small quantities, of the order of 0.5×10^{-3} to 5×10^{-3} moles per mole of available NH_2 functional group.

In practice, in order to implement the process, maleic anhydride and the diamine of formula (III) are reacted, to begin with, by operating in the chosen diluent at a temperature ranging from 30° to 100°C for a period ranging from a few minutes to 1 hour, depending on

the temperature. The dehydrating agent, the tertiary amine and, lastly, the catalyst are then added to the reaction mixture, and the mixture is then allowed to react under the temperature conditions chosen previously for a period ranging from 1 hour to 3 hours, depending on the temperature. The reaction is generally terminated by adding a nonsolvent such as water, and then the bismaleimide of formula (I) which has been prepared is isolated according to the usual methods.

By way of specific examples of bismaleimides of formula (II), there may be mentioned, in particular:

- N,N'-meta-phenylenebismaleimide,
- N,N'-para-phenylenebismaleimide,
- N,N'-4,4'-diphenylmethanebismaleimide,
- N,N'-4,4'-diphenyl ether bismaleimide,
- N,N'-4,4'-diphenylsulphonebismaleimide,
- N,N'-1,4-cyclohexylenebismaleimide,
- N,N'-4,4'-(1,1-diphenylcyclohexane)bismaleimide,
- N,N'-4,4'-(2,2-diphenylpropane)bismaleimide,
- N,N'-4,4'-triphenylmethanebismaleimide,
- N,N'-2-methyl-1,3-phenylenebismaleimide,
- N,N'-4-methyl-1,3-phenylenebismaleimide, and
- N,N'-5-methyl-1,3-phenylenebismaleimide.

These bismaleimides may be prepared according to the procedures described in US Patent US-A-3,018,290 and British Patent GB-A-1,137,290. N,N'-4,4'-diphenylmethanebismaleimide taken by itself or mixed with N,N'-2-methyl-1,3-phenylenebismaleimide, N,N'-4-methyl-1,3-phenylenebismaleimide and/or N,N'-5-methyl-1,3-phenylenebismaleimide is preferably employed in order to implement the present invention.

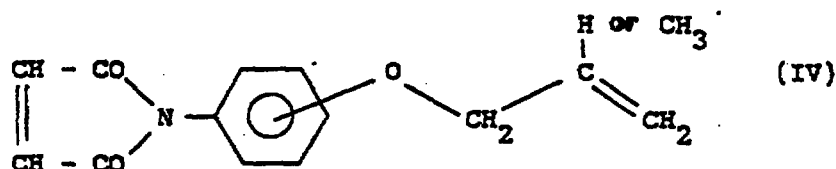
In comparison with the polyimides obtained according to French Patent FR-A-1,455,514 by heating, particularly of N,N'-4,4'-diphenylmethanebismaleimide, it has been found that the addition of an N,N'-bismaleimide containing a diorganopolysiloxane group of formula (I) to the polymerisation medium is a measure which, when these polymers are prepared in bulk, makes it possible in

particular to facilitate the transition of the maleimides into the molten state and to improve the mechanical properties markedly, increasing at least 2-fold the resilience values of the cured polymers.

5 In some cases it may be advantageous to modify the polymers according to the invention by using a copolymerisable reactant (c). As an optional reactant (c) which is suitable, there may be mentioned in particular:

10 - when it is desired, for example, to reduce the fluidity of the polymerisation medium;

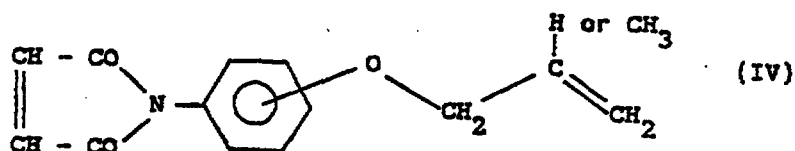
(c₁) either one or more monomers of formula:



15 in which the allyloxy or methallyloxy radical is in an ortho, meta or para position relative to the nitrogen-bonded carbon atom of the benzene ring;

(c₂) or a compound comprising:

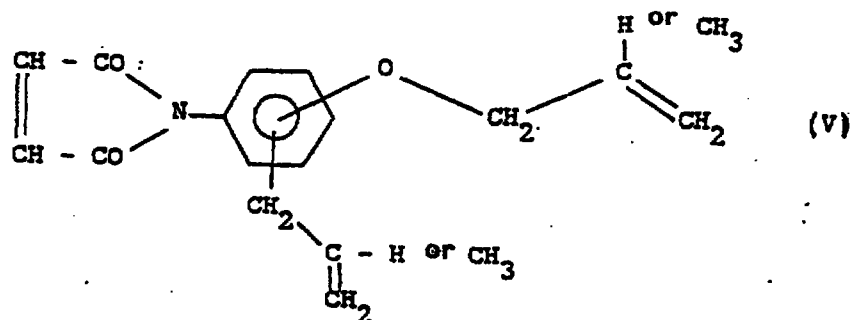
- a mixture of a monomer of formula:



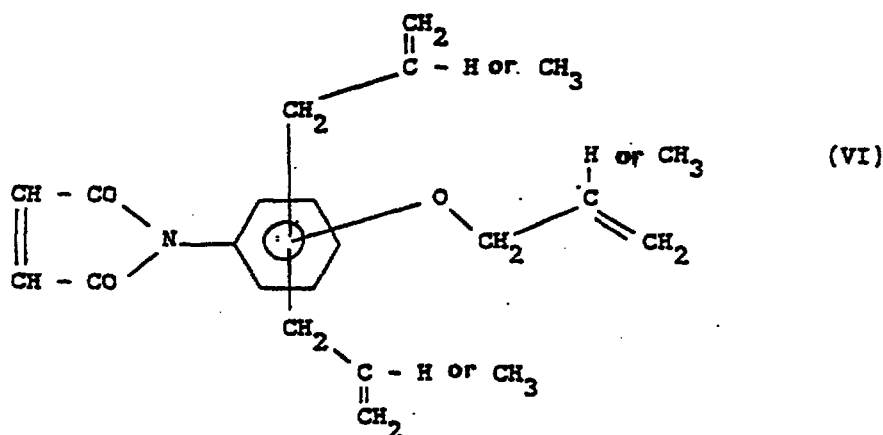
20 in which the allyloxy or methallyloxy radical is in an ortho, meta or para position relative to the nitrogen-bonded carbon atom of the benzene ring

- with

25 at least one monosubstituted derivative of formula:



and, if desired, one or more disubstituted derivatives of formula:



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In the abovementioned compound used as reactant (C₂), the proportions of the various constituents of the mixture of the products of formulae (IV), (V) and, if desired, (VI) may vary within wide limits. In general, the proportions of the constituents are chosen between the following limits (expressing the weight percentage of each of the constituents in the mixture):

- at least 30%, and preferably from 50% to 80% of N-(meth)-allyloxyphenylmaleimide of formula (IV),
- from 5% to 50% and preferably from 10% to 35% of mono-(meth)allyl substituted derivative(s) of formula (V), and
- from 0% to 20% and preferably from 0% to 15% of di(meth)allyl substituted derivative(s) of formula (VI),

it being necessary for the sum of the constituents to be equal to 100% by weight in each case.

- when it is desired, for example, to further improve the hot flexural properties:

(c₃) one or more substituted heterocycles containing one or more carbon-carbon double bonds.

5 It should be understood that mixtures of reactants (c₁) + (c₃) or (c₂) + (c₃) may be employed as reactant (c).

Regarding the optional reactant (c₁), this is chosen from:

10 - N-(2-allyloxyphenyl)maleimide,
- N-(3-allyloxyphenyl)maleimide,
- N-(4-allyloxyphenyl)maleimide,
- N-(2-methallyloxyphenyl)maleimide,
- N-(³-methallyloxyphenyl)maleimide,
15 - N-(4-methallyloxyphenyl)maleimide and mixtures of these.

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

20 Regarding the optional reactant (c₂), the crude product obtained by employing the process defined hereinafter is preferably employed as a compound comprising a mixture of N-(meth)allyloxyphenylmaleimide of formula (IV) with one or more (meth)allyl substitution
25 derivatives of formula(e) (V) and, if desired, (VI).

This process is characterised in that it consists in carrying out the following 3 stages which are linked consecutively in the same reactor:

- the first stage consists in reacting an
30 aminophenol with maleic anhydride in solvent medium by operating at a temperature ranging from 20°C to 200°C, for a period ranging, depending on the chosen temperature, from 30 minutes to 2 hours and it leads to a first reaction mixture comprising an N-(hydroxyphenyl)maleamic
35 acid;

- the second stage consists in carrying out a (meth)allylation reaction of the abovementioned acid by reacting the abovementioned first reaction mixture with a (meth)allyl halide by operating at a pH which must be

adjusted to and maintained at a constant value of between 7 and 14 by addition of a determined quantity of an alkaline aqueous solution and at a temperature ranging from 40°C to 150°C and, after acidification and removal of the aqueous phase, it leads to a second organic reaction mixture comprising an N-[(meth)allyloxyphenyl]-maleamic acid, one or more N-[(meth)allyloxy, (meth)-allylphenyl]-maleic acids and, if desired, one or more N-[(meth)allyloxy, di(meth)allylphenyl]maleamic acids;

- the third stage consists in carrying out a reaction of ring closure of the abovementioned maleamic acids by reacting the abovementioned second reaction mixture with an anhydride of a lower carboxylic acid, in the presence of a tertiary amine and, if desired, of a catalyst, and in then removing the reaction solvent, and it leads to a crude reaction product which is a compound comprising a mixture made up of: at least 30% by weight and preferably from 50% to 80% of N-(meth)allyloxyphenylmaleimide, 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 just described are linked consecutively in a single solvent for greater process simplicity, but it is possible to perform a solvent change, during one stage or another, without inconvenience. The choice of the solvent may be very wide, but, since the second stage is carried out in a hydro-organic two-phase medium, it may be desirable to employ a water-immiscible organic solvent, which considerably simplifies the treatment of the reaction mass. Among the water-miscible or immiscible solvents which may be employed preference will be given, in fact, to those which dissolve the starting aminophenol, under the temperature conditions chosen for the synthesis. Among these solvents there may be mentioned, for example: alcohols (such as, for example: methanol, ethanol,

butanol), ketones (such as, for example: acetone, methyl ethyl ketone, methyl isobutyl ketone), nitriles (such as, for example: benzonitrile, propionitrile, acetonitrile), esters (such as, for example: ethyl or butyl acetate), aromatic solvents (such as, for example: anisole, chlorobenzene), and halogenated hydrocarbons (such as, for example: chloroform, dichloromethane, dichloroethane).

Regarding the first stage of the process it may be said that the concentration of the starting reactants in the solvent employed is not critical. All the same, there is no advantage in excessive dilution for reasons of production efficiency nor in excessive concentration in order to have good stirrability. In this first stage, maleic anhydride is employed in quantities which are at least equal to one mole per mole of aminophenol; generally, larger quantities are employed, which are of the order of 1.01 to 1.5 moles per mole of aminophenol. Furthermore, the temperature is preferably between 40°C and 60°C.

Regarding the second step, this is begun by adding to the reaction mixture the quantity of an alkaline aqueous solution, for example of an aqueous NaOH solution, which is necessary, on the one hand, in order to form a salt of N-(hydroxyphenyl)maleamic acid and, on the other hand, in order to obtain the desired pH. The pH should be kept constant throughout the reaction by the addition of sodium hydroxide; preferably, the pH is adjusted and maintained at a constant value of between 10 and 12. The allylation reaction is preferably carried out using (meth)allyl bromide or chloride. The quantity of (meth)allyl halide is of the order of 1.5 to 10 moles per phenolic OH molar group and, preferably, of the order of 2 to 4. The excess of the reactant may be recovered at the end of the run and recycled into a subsequent run. The time taken to run in the (meth)allyl halide is not critical and may lie in 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 using usual acids, preferably inorganic oxyacids or hydric acids. The aqueous layer is removed and the organic layer is left in the reactor.

5 Regarding the third stage of the process, acetic anhydride is advantageously employed as an anhydride of a lower carboxylic acid, in quantities at least equal to one mole per HOOC-CH=CH-CO-NH molar group to be cyclised. Generally, larger quantities are employed, which are of
10 the order of 1.05 to 1.5 moles per maleamic group.

 Among suitable tertiary amines, trialkylamines and N,N-dialkylanilines in which the alkyl radicals contain from 1 to 12 carbon atoms may be mentioned in particular. Triethylamine and N,N-dimethylaniline are
15 advantageous in use. The quantities of tertiary amine are between 0.05 and 2 moles per HOOC-CH=CH-CONH- molar group.

 The catalysts which may be employed are, for example, nickel salts of carboxylic acids, hydrated if
20 desired, as well as the chelated forms of this metal. The acetate and the acetylacetonate are particularly suitable. These catalysts are employed in very small quantities, of the order of 0.05 to 1.5 g per HOOC-CH=CH-CO-NH- molar group and, preferably, of the
25 order of 0.1 to 0.8 g.

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

 In accordance with a highly preferred way of implementation, the abovementioned process can be applied
35 well, starting from meta-aminophenol, to the preparation of compounds comprising mixtures based on: N-[3-(meth)allyloxyphenyl]maleimide + N-[3-(meth)allyloxy-4-(meth)allylphenyl]maleimide + N[3-(meth)allyloxy-6-(meth)allylphenyl]maleimide + if desired N-[3-(meth)allyloxy-4,6-

di(meth)allylphenyl]maleimide.

It should be noted that starting with ortho-amino-phenol leads to compounds comprising mixtures based on:

5 N-[2-(meth)allyloxyphenyl]maleimide + N-[2-(meth)-allyloxy-3-(meth)allylphenyl]maleimide + N-[2-(meth)-allyloxy-5-(meth)allylphenyl]maleimide + if desired N-[2-(meth)allyloxy-3,5-di(meth)allylphenyl]maleimide. It

10 should further be noted that starting with para-aminophenol leads to compounds comprising mixtures based on:

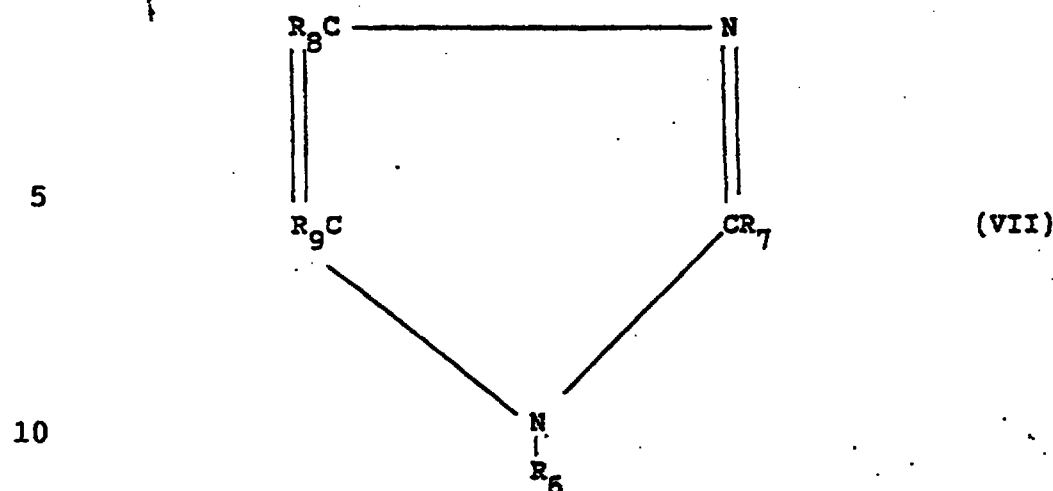
N-[4-(meth)allyloxyphenyl]maleimide + N-[4-(meth)allyloxy-3-(meth)allylphenyl]maleimide + if desired N-[4-(meth)-allyloxy-3,5-di(meth)allylphenyl]maleimide

15 Regarding the optional reactant (c₃), this is chosen from: vinylpyridines, N-vinylpyrrolidone, allyl isocyanurate, triallyl isocyanurate and vinyltetrahydrofuran.

20 The reactivity of the constituents (a), (b) and, if desired, (c) of the polymerisation mixture according to the invention may be increased, for example when the envisaged applications call for mechanical injection moulding operations to be carried out, by the addition of a catalyst (d) which may be either (d₁) a radical polymerisation initiator such as, for example, dicumyl peroxide, lauroyl peroxide or azobisisobutyronitrile, or

25 (d₂) an imidazole compound.

The said imidazole compound (d₂) corresponds to the general formula:



15 in which each of R_6 , R_7 , R_8 and R_9 , which are identical or different, denotes: a hydrogen atom, an alkyl or alkoxy radical containing from 1 to 20 carbon atoms or a vinyl, phenyl or nitro radical, it being possible for R_8 to form a single ring, such as, for example, a benzene ring, with R_9 and the carbon atoms to which these radicals are linked, it being also possible for R_6 to denote a carbonyl group linked to a second imidazole ring.

20 As specific examples of imidazole compounds (d_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.

25 In the heat-stable polymers which have just been defined, the quantities of reactants (a) and (b) are chosen so as to give, by weight relative to the total weight of the constituents:

- 30 - from 2 to 50%, and preferably from 5 to 20%, of bis-maleimide of formula (I),
 - from 50 to 98%, and preferably from 80 to 95%, of bis-maleimide(s) of formula (II).

35 Regarding the quantity of the optional reactant (c), this generally represents less than 60%, and preferably from 5% to 50%, of the total weight of the reactants (a) + (b).

Regarding the catalyst (d), depending on its nature and according to the desired polymerisation rate

in the application stage, this is employed in a proportion lying in the range from 0.01 to 1% by weight relative to the total of the reactants (a) + (b) + if desired (c) and, preferably, ranging from 0.05 to 0.5%.

5 The polymers according to the invention may be prepared by direct heating of the reactant (a), of the reactant (b) and, if desired, of the reactant (c) with, if need be, the catalyst (d) at least until a homogeneous liquid mixture is obtained. The temperature may vary as
10 a function of the physical state of the compounds present, but it is generally between 50°C and 300°C. It is advantageous to put and to maintain the starting compounds in an intimately mixed state before and during heating, for example by means of good stirring. When the
15 compound (d) is employed, it is preferably added at the outset to the well-stirred reaction mixture containing the reactants (a) and/or (b). When this compound is particularly active, in order to avoid its encapsulation in the polymer network produced, it is desirable to add
20 it in a solvent or diluent which is compatible with the reaction mixture; it has been found that it could be advantageous to employ one of the polar organic liquids which are discussed hereinafter, as a solvent or diluent.

 The preparation of the polymers according to the
25 invention may also be carried out by heating the mixture of the reactants in an organic diluent which is liquid in at least a part of the range 50°C - 250°C. Among these diluents, particular mention may be made of aromatic hydrocarbons such as xylenes and toluene, halogenated
30 hydrocarbons such as chlorobenzenes, polar solvents such as dioxane, tetrahydrofuran and dibutyl ether, dimethylformamide, dimethyl sulphoxide, N-methylpyrrolidone, dimethylacetamide, methylglycol and ethyl ethyl ketone. The polymer solutions or suspensions may be employed as
35 such for many applications; the polymers may also be isolated, for example by filtration, if desired after precipitation by means of an organic diluent which is miscible with the solvent employed. In this context, a hydrocarbon whose boiling point does not markedly exceed

120°C may be advantageously employed.

It should be understood that the properties of the polymers according to the invention can vary to a large extent, particularly as a function of the precise nature of the reactants employed, of the proportions of reactants which are chosen and of the precise temperature conditions which are chosen in the abovementioned range. Insofar as the polymers which are obtained are concerned, the latter may be cured polymers, insoluble in the usual solvents, such as, for example, the compounds mentioned in the preceding paragraph and exhibiting no appreciable softening below the temperature at which they begin to degrade.

However, these polymers may also have the appearance of prepolymers (P) soluble in polar organic solvents and exhibiting 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 the reactants until a homogeneous or pasty product is obtained at a temperature which is generally between 50°C and 180°C before a period which may range from a few minutes to a few hours, this period being proportionally shorter the higher the temperature chosen. Before the mixture of the reactants is subjected to heating, it is advantageous, again, to ensure that it is first intimately mixed by stirring. Here again there is a preferred method of employing the compound (d) and it is that indicated hereinbefore in connection with the direct preparation of cured polymers. The preparation of the prepolymers may also be carried out in suspension or in solution in a diluent which is liquid in at least a part of the range 50°-180°C.

In the case where it is chosen to resort to the optional reactant (c), it should be noted that these prepolymers (P) may also be obtained by forming, from the reactant (a) and the reactant (c), a prepolymer (PP) which is then reacted with the reactant (b) and, if need be, the compound (d). A prepolymer (P'P') may also be prepared beforehand by heating the mixture of reactant

(b), of reactant (c) and, if need be, of compound (d), and then reacting it with the reactant (a) in order to obtain the prepolymer (P). The temperature and time conditions which are employed for the preparation of the prepolymers (PP) or (P'P') and for their conversion into prepolymers (P) are those indicated hereinbefore in connection with the preparation of the prepolymers (P) by direct mixing of the reactants (a), (b) and, if desired, (c) with, if need be, the compound (d).

The prepolymers (P) may be employed in the form of a liquid mass, mere hot casting being sufficient in order to form and to produce moulded objects. They may also be employed, after cooling and milling, in the form of powders which are remarkably amenable to compression moulding operations, if desired in the presence of fillers in powder, sphere, granule, fibre or flake form. The pre-polymers (P) may be employed in the form of suspensions or of solutions for producing coatings and preimpregnated intermediate articles in which the reinforcement may consist of fibrous materials based on aluminium or zirconium silicate or oxide, carbon, graphite, boron, asbestos or glass. These prepolymers (P) may also be employed for the production of 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° and 250°C; an additional forming may be carried out during the curing, if desired under vacuum or under superatmospheric pressure, it being possible for these operations also to be consecutive.

In the case where it is chosen to resort to the optional reactant (c), it is not a departure from the scope of the invention to prepare the polymers according to the invention which do not have the appearance of prepolymers (P), by using an intimate mixture of prepolymer (PP), of reactant (b) and, if need be, of compound (d) or of an intimate mixture of prepolymer (P'P') and of reactant (a) which are heated in bulk in the conditions

described above.

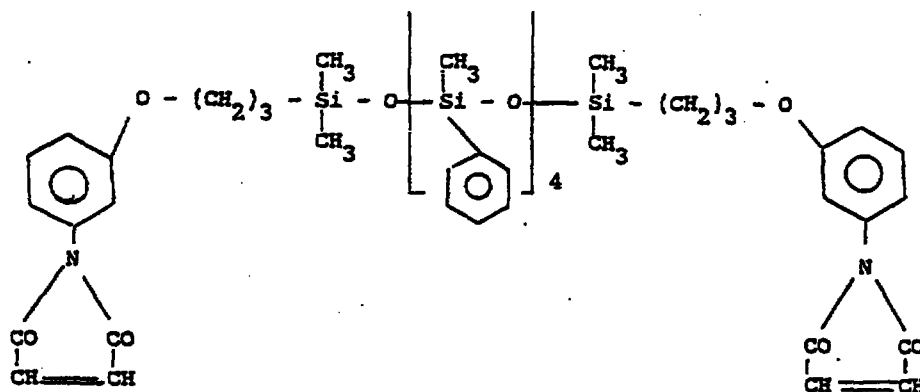
The prepolymers according to the invention are of interest to the industrial sectors which require materials endowed with good mechanical and electrical properties, as well as a high chemical inertness at temperatures of 200°C to 300°C. By way of examples, they are suitable for the manufacture of plate or tubular insulators for electrical transformers, printed circuit boards, pinions, rings, and the like. The preimpregnated articles can be employed for the production of components of various shapes and functions in many industries such as, for example, in aeronautics. These components, known as laminates, which may be components of revolution, are obtained by laying down several layers of prepregs on a former or a support. The prepregs may also be employed as reinforcement or as means of repairing damaged components. It is also possible to imagine articles according to the filament winding techniques with or without a support; and it is also possible to perform injection moulding or pultrusion. It will be recalled that, for example, in order to make moulded objects, it is possible to start either with the mixture of the reactants or with a prepolymer (P). When starting directly from the mixture of the reactants, this mixture is given the shape of the desired object and curing is then carried out by heating. When starting with the prepolymer (P), this may be moulded merely by hot casting or by injection and its cure is then produced by heating.

The following examples are given by way of illustration but without a limitation being implied.

EXAMPLE 1

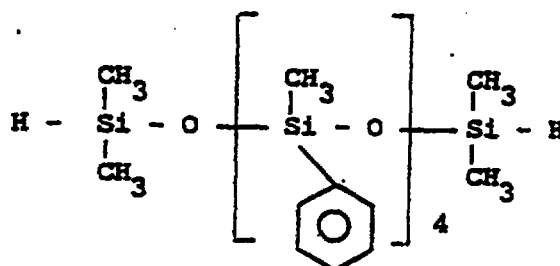
1. Description of the process for preparing the bismaleimide containing a diorganopolysiloxane group employed in this example having the following formula:

1.1 Preparation of the diamine containing a diorganopolysiloxane group from which this bismaleimide



is derived:

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



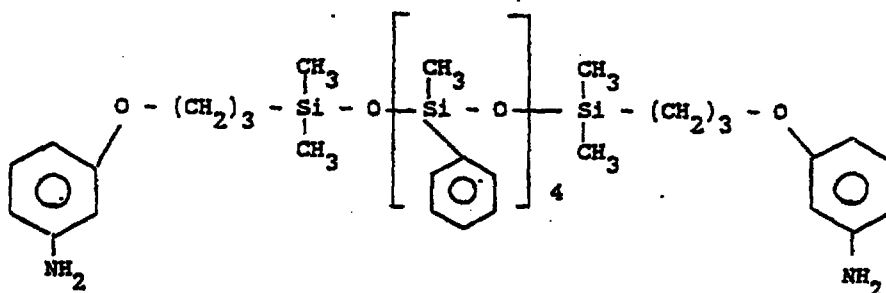
which has a molecular mass of the order of 678 g.

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

137 g (0.92 mole) of meta-allyloxylaniline are then run in gradually into the reactor, over a period of 60 minutes, so as to control the exothermicity of the reaction (the temperature is maintained at 55°C). Thirty

minutes after the end of the addition, ambient temperature is regained.

The product obtained, 448.9 g in weight, is a clear viscous oil, orange-brown in colour, which exhibits a proton NMR spectrum in agreement with the structure:



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

1.2 Preparation of the diorganopolysiloxane-bismaleimide:

The following are introduced simultaneously, over 10 minutes, with the aid of 2 dropping funnels, into a glass reactor equipped with central stirring and with 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 an acetone solution of 25 g (0.025 mole and 0.05 NH₂ functional group) of the siloxane diamine prepared in paragraph 1.1.,

- 15 cm³ of an acetone solution of 6.4 g (0.055 mole) of maleic anhydride.

When the additions have been completed, each dropping funnel is rinsed with 5 cm³ of acetone, which is then added to the reaction mass, kept stirred for a further 15 minutes.

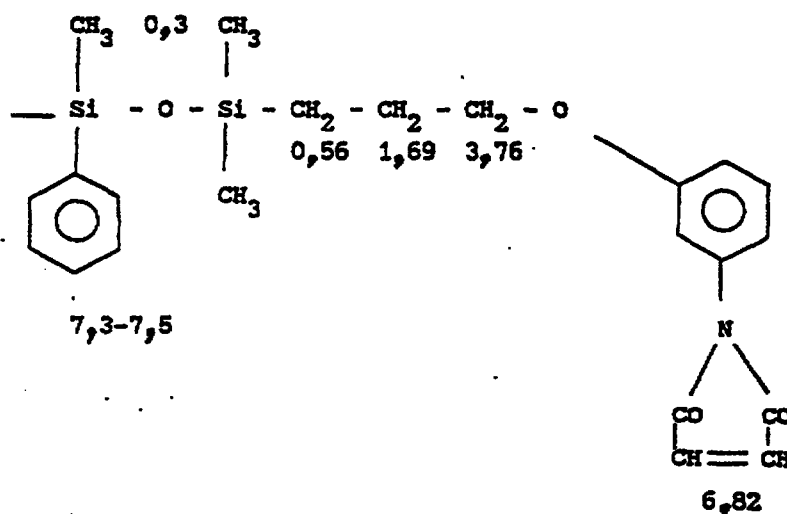
6.1 g (0.06 mole) of acetic anhydride are charged into the dropping funnel which contained maleic anhydride,

and 1.67 g (0.0165 mole) of triethylamine into the other funnel.

These two compounds are then run into the reactor and 0.3 cm³ of an aqueous solution containing 0.0528 mole of nickel acetate per 100 cm³ of solution is then added.

The reaction mixture is refluxed with stirring for 2 hours 30 minutes. The temperature is then reduced to 20°C.

The reaction mixture is diluted with 80 cm³ of iced water (5°C) with vigorous stirring and the oily product present is then extracted with 80 cm³ ethyl acetate. The organic phase obtained is washed with three 80 cm³ portions of water in order to attain a pH of 6 in the washes, and is then dried for 2 hours over anhydrous sodium sulphate. After filtration, ethyl acetate is removed by evaporation from the organic phase, this operation being finished under reduced pressure (approximately 70 Pa) at 60°C and 27.3 g (i.e. a weight yield of 96% relative to theory) of a viscous, orange-brown product are collected, whose NMR spectrum agrees with the structure of the desired bismaleimide, which was defined at the beginning of this example. The molecular mass is of the order of 1136 g [sic]. In proton NMR (solvent: CDCl₃ [sic]; reference: tetramethylsilane), the absence of the starting diamine is noted and the following chemical shifts, expressed in ppm, are noted:



The ratio:
$$\frac{\text{number of Si-phenyl bonds}}{\text{number of Si-methyl bonds}}$$

is found to be equal to 0.5.

In infrared spectrometry, the presence of the following bands is noted: $\nu(\text{imide C=O}) = 1710 - 1730 \text{ cm}^{-1}$;
 $\nu(\text{maleimide C-N-C}) = 1160 \text{ cm}^{-1}$; $\nu(\text{C-N-C}) = 1400 \text{ cm}^{-1}$

2. Description of a heat-stable polymer in accordance with the present invention:

9.6 g of the bismaleimide containing a diorganopolysiloxane group which is described in Example 4 are introduced into a glass reactor equipped with a degassing side-arm and with an anchor-type stirrer and immersed in an oil bath preheated to 160°C . After 2 minutes' stirring, 70.4 g of N,N'-4,4'-diphenylmethane-bismaleimide are then added over 8 minutes. The mixture is allowed to react while being stirred for 15 minutes, the last 5 of which are performed at a reduced pressure of $13.3 \times 10^2 \text{ Pa}$.

The reaction mass, clear in appearance, is then cast into a mould preheated to 150°C with the objective of preparing plaques $140 \times 100 \times 4 \text{ mm}$ in size, which will be subjected to the following cure cycle:

10 minutes at 160°C ,
130 minutes between 160° and 250°C ,
16 hours at 250°C , and
2 hours between 250°C and 25°C .

After demoulding, the plaques based on cured, brown and translucent polymer are cut up so as to produce specimens $60 \times 10 \times 4 \text{ mm}$ in size on which unnotched Charpy impact tests are carried out according to the NFT Standard 51,035. The resilience at 25°C obtained in this manner is 3.4 kJ/m^2 .

By way of a comparative test, the operations described hereinbefore have been reproduced by charging only 100 g of N,N'-4,4'-diphenylmethanebismaleimide into the reactor, preheated to 175°C . Reaction is allowed to take place with stirring for 12 minutes, 5 of which are carried out at a reduced pressure of $6.65 \times 10^2 \text{ Pa}$.

The cure cycle for the plaques moulded at 200°C is the following:

1 hour 45 minutes at 200°C,
1 hour between 200°C and 250°C,
16 hours at 250°C, and
2 hours between 250°C and 25°C.

5 The resilience at 25°C, measured on the
specimens, is 1.7 kJ/m².

EXAMPLE 2

10 Into a glass reactor equipped with an anchor-type
stirrer and with a side-arm permitting the deposition of
volatile products, are introduced, at ambient temperature:
- 18 g of N-(3-allyloxyphenyl)maleimide (0.0786 mole),
and
- 0.0907 g of imidazole.

15 The mixture is homogenised by stirring and 10.8 g
of the bismaleimide containing a diorganopolysiloxane
group which is described hereinbefore in Example 1 are
added. The reactor is then immersed in an oil bath
preheated to 160°C. After 2 minutes' stirring, 61.2 g of
20 N,N'-4,4'-diphenylmethanebismaleimide (0.171 mole) are
then added over 3 minutes to the stirred mixture. The
reaction mass is then allowed to react for 6 minutes.
The temperature is then lowered to 150°C over 5 minutes
and a reduced pressure of approximately 1.33×10^2 Pa is
25 applied for 2 minutes, and then atmospheric pressure is
regained, at which the reaction mass is stirred for a
further 3 minutes.

30 This mass is then cast in a mould preheated to
150°C in order to prepare plaques 140 x 100 x 4 mm in
size, which will be subjected to the following cure
cycle:

10 minutes between 150°C and 250°C,
16 hours at 250°C, and
2 hours between 250°C and 25°C.

35 After demoulding, some of the plaques obtained
based on cured, brown and opaque polymer are cut up in
order to obtain specimens 30 x 7 x 4 mm in size which are
used for measuring the flexural strength (Sf) and modulus
(Mf) (Instron apparatus with a distance of 25.4 mm

between supports). The values of the flexural mechanical properties are collated in the following table:

Sf in MPa				Mf in MPa			
Initial		after 1000 hours at 250°C		Initial		after 1000 hours at 250°C	
at 25°C	at 250°C	at 25°C	at 250°C	at 25°C	at 250°C	at 25°C	at 250°C
140	81	115	55	2600	2100	2600	2200

Using DMA ("Dynamic Mechanical Analysis") it is found that the flexural modulus is maintained very well with temperature up to 350°C.

The remaining plaques obtained earlier are cut up to give:

- specimens of the type of those described hereinbefore in Example 1, on which unnotched Charpy impact tests are carried out; the resilience at 25°C is found to be equal to 8.3 kJ/m²;

- specimens known as C.T. ("Compact Tension") specimens according to the specifications of the ASTM Standard E 399 which are used for measuring the intrinsic mechanical parameters of the material, consisting of the concentration coefficient of critical stress in cracking mode 1 (K_{1c}) and of the rate of restoration of critical energy in cracking mode 1 (G_{1c}) (these parameters are used to evaluate the ability of the material to withstand crack propagation under the effect of an impact):

$$K_{1c} = 0.41 + 0.1 \text{ MP}\sqrt{\text{am}}$$

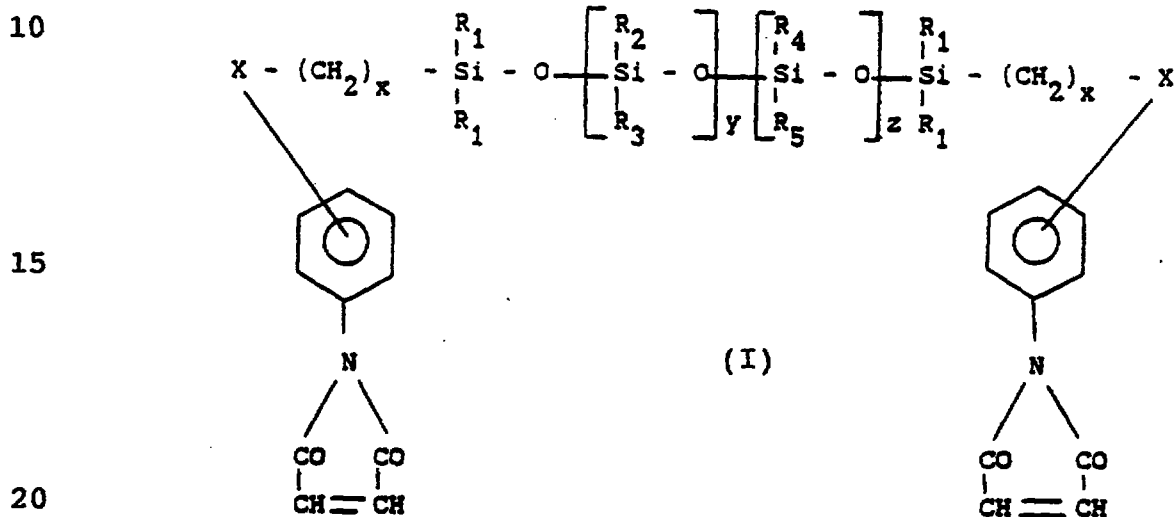
$$G_{1c} = 60 \pm 5 \text{ J/m}^2.$$



CLAIMS

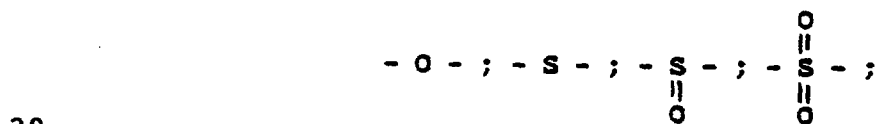
1. Polymers containing imide groups, characterised in that they comprise the product of reaction, at a temperature ranging from 50° to 300°C, between:

- 5 - (a) 2 to 50% relative to the total weight of (a) + (b) of an N,N'-bismaleimide containing a diorganopolysiloxane group corresponding essentially to the general formula:



in which

- 25 - X, which is in an ortho, meta or para position relative to the nitrogen-bonded carbon atom of the benzene ring, denotes an atom or group as follows:



- 35 - each of R₁, R₂, R₃, R₄ and R₅, which are identical or different, denotes a monovalent hydrocarbon radical chosen from: linear or branched alkyl radicals containing from 1 to 12 carbon atoms, it being possible for these radicals to be substituted by one or more chlorine, bromine or fluorine atoms or by a -CN group; a phenyl radical substituted, if desired, by one or more alkyl and/or alkoxy radicals containing from 1 to 4



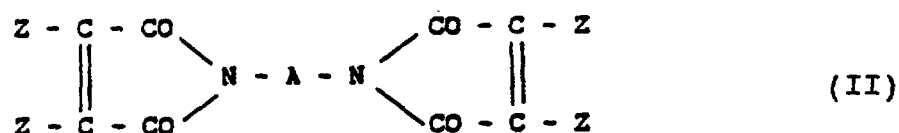
carbon atoms or by one or more chlorine atoms;

- the symbol x is an integer situated in the range from 2 to 8;

5 - the symbols y and z denote identical or different, whole or fractional numbers whose sum is situated in the range from 0 to 100;

- (b) 50 to 98% relative to the total weight of the constituents (a) + (b) of an N,N'-bismaleimide or a combination of a number of bismaleimides of formula:

10



15

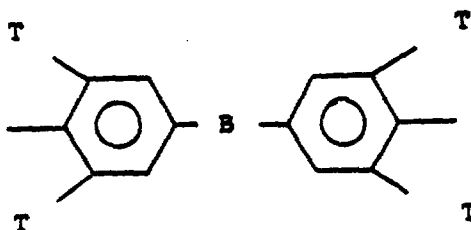
in which

- each of the symbols Z, which are identical or different, denotes H, CH₃ or Cl,

20

- the symbol A denotes a divalent radical chosen from the group consisting of cyclohexylene, phenylene, 4-methyl-1,3-phenylene, 2-methyl-1,3-phenylene, 5-methyl-1,3-phenylene and 2,5-diethyl-3-methyl-1,4-phenylene radicals, and the radicals of formula:

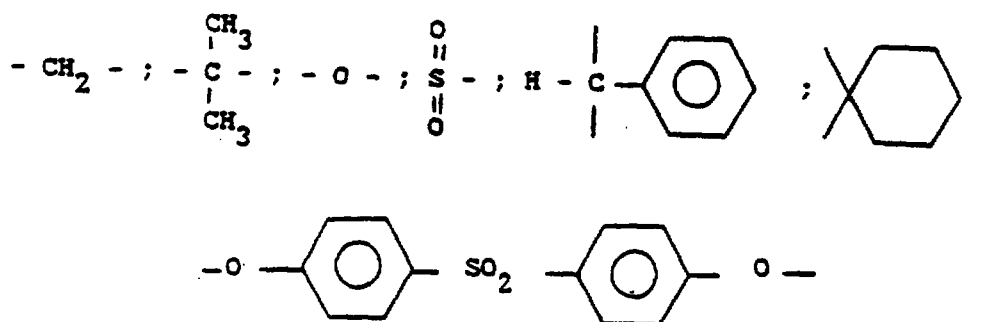
25



30

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

35





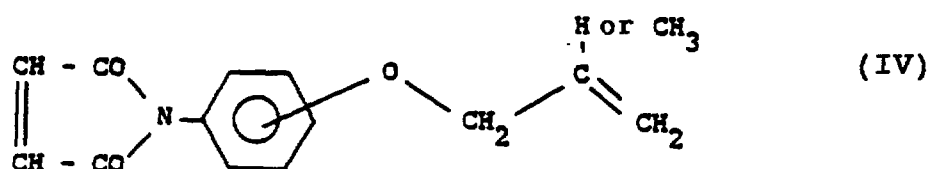
and each of the symbols T, which are identical or different, denotes a hydrogen atom or a methyl, ethyl or isopropyl radical;

- (c) if desired, one or more monomers other than a bismaleimide of formula (I) or of formula (II) and containing one or more polymerisable carbon-carbon double bonds; and

- (d) a catalyst, if desired.

2. Polymers according to Claim 1, characterised in that the reactant (c), when one of such is employed, consists of the following species:

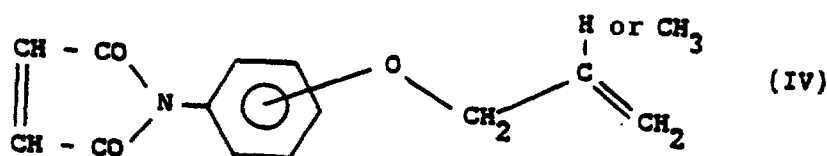
(C₁) either one or more monomers of formula:



20 in which the allyloxy or methallyloxy radical is in an ortho, meta or para position relative to the nitrogen-bonded carbon atom of the benzene ring;

(C₂) or a compound comprising:

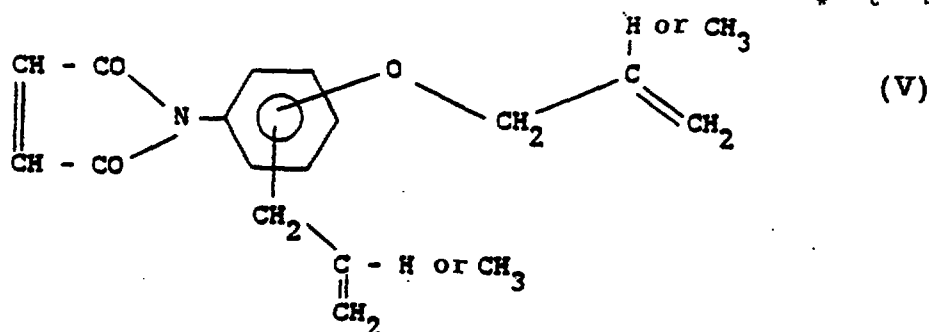
- a mixture of a monomer of formula:



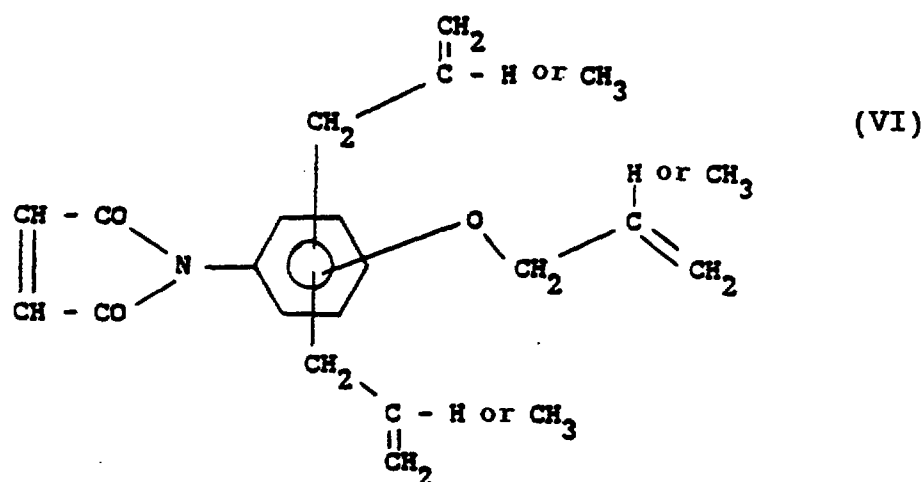
30 in which the allyloxy or methallyloxy radical is in an ortho, meta or para position relative to the nitrogen-bonded carbon atom of the benzene ring,

- with:

35 - at least one monosubstituted derivative of formula:

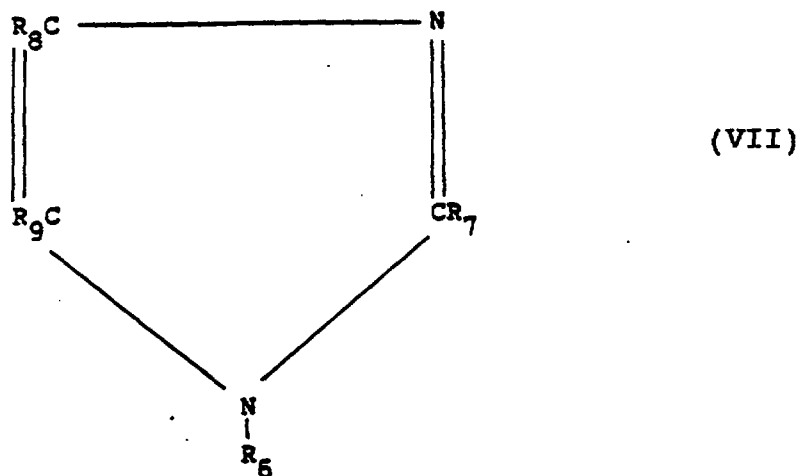


- and, if desired, one or more disubstituted derivatives of formula:



(C₃) or one or more substituted heterocycles containing one or more carbon-carbon double bonds..

3. Polymers according to either of Claims 1 and 2, characterised in that the catalyst (d), when one of such is employed, is either (d₁) a radical polymerisation initiator, or (d₂) an imidazole compound of formula





in which each of R_6 , R_7 , R_8 and R_9 , which are identical or different, denotes: a hydrogen atom, an alkyl or alkoxy radical containing from 1 to 20 carbon atoms or a vinyl, phenyl or nitro radical, it being possible for R_8 to form a single ring such as, for example, a benzene ring, with R_9 and the carbon atoms to which these radicals are linked, it being also possible for R_6 to denote a carbonyl group linked to a second imidazole ring.

4. Polymers according to any one of Claims 1 to 3, characterised in that the quantities of reactants (a) and (b) are chosen so as to give, by weight relative to the total weight of these constituents:

- from 5 to 20% of bismaleimide of formula (I),
- from 80 to 95% of bismaleimide(s) of formula (II).

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

6. Polymers according to any one of Claims 1 to 5, characterised in that the optional catalyst (d) is employed in a proportion lying in the range from 0.01 to 1% by weight relative to the total of the reactants (a) + (b) + if desired (c) and, preferably, ranging from 0.05 to 0.5%.

7. Polymers according to any one of Claims 1 to 6, characterised in that they are in the form of cured polymers, insoluble in the usual solvents and exhibiting no appreciable softening below the temperature at which they begin to degrade.

8. Polymers according to any one of Claims 1 to 6, characterised in that they are in the form of heat-curable prepolymers (P) soluble in polar organic solvents and exhibiting a softening point at a temperature below 200°C.

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 while operating 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 between 50°C and 180°C in order to form a prepolymer (P) in a first stage, and then to cause the curing of the prepolymer (P) by heating to a temperature of between 150°C and 250°C.

11. Process for preparing heat-curable 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 while operating in bulk or in an organic diluent.

12. Preparation process according to any one of Claims 9 to 11, characterised in that, when the operation is carried out in bulk, the reactant (a) which is employed is the bismaleimides of formula (I) in which the ratio:

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

is at least equal to 0.25.

13. Application of the polymers according to any one of Claims 1 to 8 to the manufacture of moulded objects, of coatings, of articles of cellular structure and of reinforced and impregnated composite materials.