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(54) **COATING, ADHESIVE AND SEALANT COMPOSITIONS**

BESCHICHTUNGS-, KLEBE- UND DICHTMITTEL ZUSAMMENSETZUNGEN
COMPOSITIONS DE REVETEMENT, ADHESIVES ET D'ETANCHEITE

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- (56) References cited:
EP-A- 0 580 328 **US-A- 4 122 074**

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Description**Field of the invention**

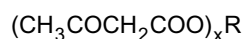
5 [0001] This invention relates to coating, adhesive and sealant compositions curable by Michael reaction, that is by addition of an anion derived from a nucleophilic group, for example a carbanion, to an activated carbon-carbon double bond. This involves reaction between (A) a Michael acceptor which is a compound or polymer generally containing at least two activated olefinic double bonds and (B) a Michael donor which is a compound or polymer containing at least one and generally containing at least two nucleophilic groups.

Background art

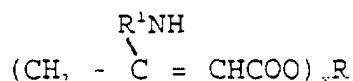
10 [0002] Coating compositions curable by Michael reaction are disclosed in US-A-4408018, GB-A-2048913, US-A-4602061, US-A-5084536, US-A-5169979, EP-A-697444 and US-A-4730033. In general, the Michael donor in these compositions is a compound having at least two activated methylene groups, for example acetoacetate groups, or a polyamine or polythiol.

[0003] US-A-4588807 describes a benzylidenemalononic acid polyester and its use for the UV stabilisation of thermoplastics.

15 [0004] EP-A-599478 describes a coating or impregnating composition comprising an aqueous dispersion of a vinyl addition polymer and a reactive coalescent of the formula:



20 or



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where R is an organic radical of valency $x=1-6$ and R^1 is H or alkyl.

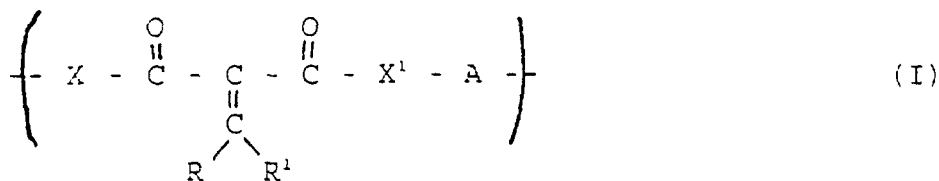
[0005] US-A-5451653 describes improved crosslinking systems for coatings and adhesives comprising a crosslinkable polymer having activated ketomethylene (e.g. acetoacetate) groups and an aldimine curing agent.

30 [0006] US-A-5426156 describes a two-component binder system comprising a CH-acid component that is a polymer with at least two enamine functions in the molecule and a compound containing at least two alpha, beta-unsaturated ester or amide groups.

35 [0007] Coating and sealant compositions curing by Michael reaction have several advantages. Liquid polymers and oligomers can be crosslinked to form tough hard coatings, so that the coating composition need have little or no volatile organic solvent to achieve a viscosity suitable for spray application. The reactive groups involved in curing are less of a health and/or safety risk than most crosslinkable reactive groups. The cured materials are generally resistant to hydrolysis and degradation, particularly in the case where the Michael donor is an activated methylene group since the new bonds formed on crosslinking are C-C bonds. Ester linkages, such as acetoacetates, acquire greater steric hindrance and hence hydrolysis resistance as a result of the Michael crosslinking reaction. The Michael reaction is beneficial for water-borne systems because it involves the transfer of hydrogen (as a proton) from a more electronegative element (with potential for hydrogen bonding) to a less electronegative element, carbon, which is not capable of hydrogen bonding. The reaction mixture therefore becomes less polar during curing, and in a coating the affinity for water should consequently decrease as curing progresses. In some cases, a water-soluble polymer/crosslinker system can be transformed into a water-resistant cured coating upon crosslinking. There is, however, a need for Michael curing coatings which cure more rapidly, particularly at ambient temperature, and/or are capable of curing without the need for powerful alkaline catalysts.

Disclosure of invention

40 [0008] According to one aspect of the invention, a coating, adhesive or sealant composition curable by Michael reaction comprises (A) a Michael acceptor which is a compound or polymer containing at least two activated olefinic double bonds and (B) a Michael donor which is a compound or polymer containing at least two nucleophilic groups and is characterised in that the Michael acceptor (A) is a polymer having repeating units of the formula:-



where R is hydrogen or an alkyl or aryl group which is optionally substituted and R¹ is hydrogen or an alkyl group which is optionally substituted;

X and X¹ are each selected from an oxygen atom and a group of the formula



where R² is hydrogen or an alkyl or aryl group which is optionally substituted; and

A is a divalent organic group.

[0009] The alkyl groups mentioned above and throughout the remainder of the text may for example have up to 12 carbon atoms, preferably up to 4 or 6 carbon atoms, for example methyl or ethyl. The aryl groups mentioned above and throughout the remainder of the text may for example have 6 to 12 carbon atoms and are preferably phenyl. The alkylene and arylene groups referred to below and throughout the remainder of the text may be similarly defined except for being divalent instead of monovalent. Substituents for all such groups which may be mentioned are halogen, hydroxyl and other non-reactive groups. The divalent organic group A is linked to X¹ through a carbon atom. It may for example be an alkylene or arylene group which is optionally substituted.

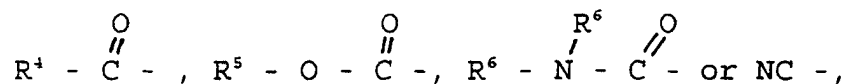
[0010] According to another aspect of the invention a coating, adhesive or sealant composition curable by Michael reaction comprises (A) a Michael acceptor which is a compound or polymer containing at least two activated olefinic double bonds and (B) a Michael donor which is a compound or polymer containing at least two nucleophilic groups and is characterised in that the Michael acceptor (A) is a compound or polymer containing at least two groups of the formula:-



where A¹ is a divalent organic group or a linking bond whereby the group (II) is linked to the compound or polymer (A);

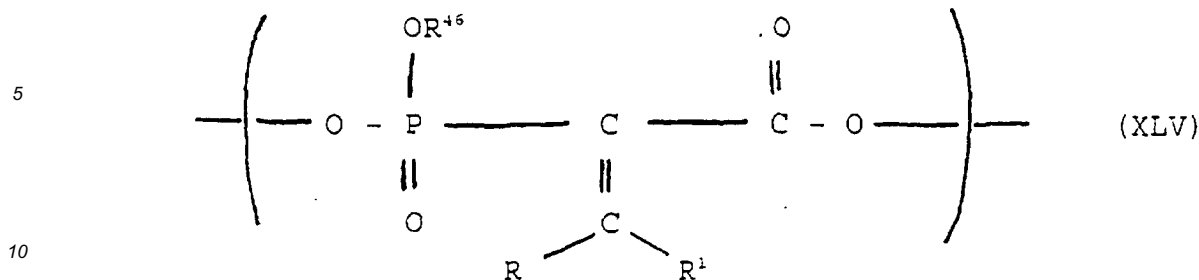
R³ is hydrogen or an alkyl group; and

E and E¹ are each electron-withdrawing groups independently selected from groups of the formula:



where R⁴ and R⁵ each represent an optionally substituted alkyl or aryl group and each group R⁶ represents a hydrogen atom or an optionally substituted alkyl or aryl group.

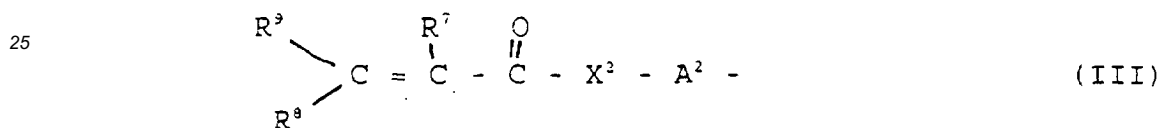
[0011] According to another aspect of the invention, a coating, adhesive or sealant composition curable by Michael reaction comprises (A) a Michael acceptor which is a compound or polymer containing at least two activated olefinic double bonds and (B) a Michael donor which is a compound or polymer containing at least two nucleophilic groups and is characterised in that the Michael acceptor (A) is a compound or polymer containing at least two groups of the formula:-



where R and R¹ are defined as in formula (I) above and R⁴⁶ is an alkyl or aryl group which is optionally substituted.

15 **[0012]** We have found that the polymers of formula (I), (II) or (XLV), in which the olefinic C=C bond is doubly activated by having two electron-withdrawing groups on one of the carbon atoms at the C=C bond, are substantially more reactive in Michael curing systems than are polymers containing acrylate or methacrylate ester groups.

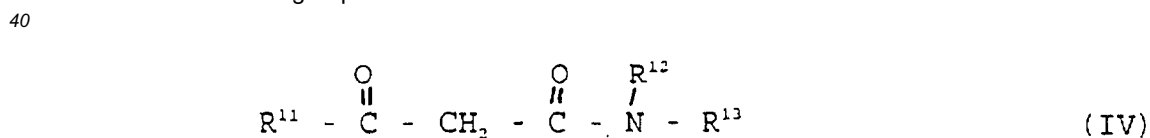
20 **[0013]** According to another aspect of the invention, a coating, adhesive or sealant composition curable by Michael reaction comprises (A) a Michael acceptor which is a compound or polymer containing at least two activated double bonds and (B) a Michael donor which is a compound or polymer containing at least two nucleophilic groups and is characterised in that the Michael acceptor (A) is a compound or polymer containing at least two doubly activated olefinic groups of the formula:



30 where R⁷ is an electron-withdrawing group, R⁸ and R⁹ are each independently selected from hydrogen, alkyl, which is optionally substituted, and aryl, which is optionally substituted; X² is an -O- or

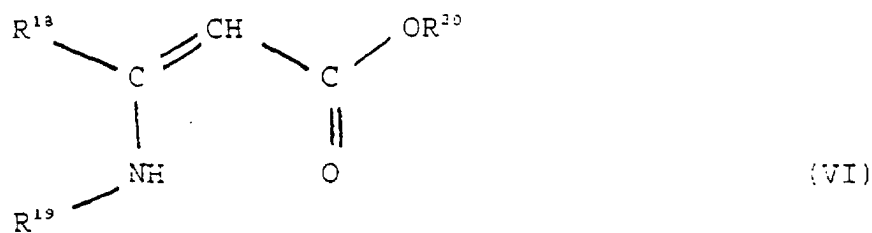


group, where R¹⁰ is hydrogen or an alkyl group; and A² is an optionally substituted alkylene group linking the doubly activated olefinic group to the compound or polymer (A); and in that the nucleophilic groups of the Michael donor (B) are beta-ketoamide groups of the formula:



where at least one of the groups R¹¹, R¹² and R¹³ is an optionally substituted alkylene or arylene radical whereby the ketoamide group is linked to the compound or polymer (B) and the remaining groups R¹¹, R¹² and R¹³ are in the case of R¹¹ an optionally substituted alkyl or aryl group and in the case of R¹² and R¹³ a hydrogen atom or an optionally substituted alkyl or aryl group, provided that at least one of R¹² and R¹³ is other than aryl and arylene; or

50 (ii) enamine beta-carboxylate groups of the formula:



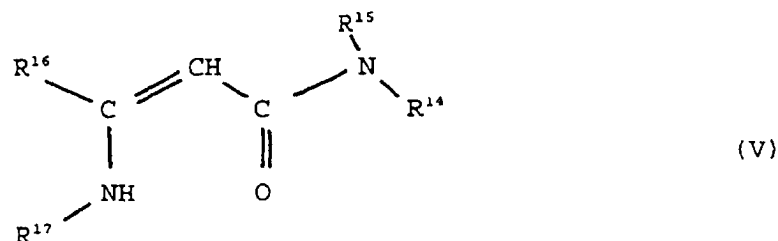
where at least one of the groups R^{18} , R^{19} and R^{20} is an optionally substituted alkylene radical or R^{18} is an optionally substituted arylene radical, whereby the enamine beta-carboxylate group is linked to the compound or polymer (B), and of the remaining groups R^{18} is a hydrogen atom or an optionally substituted alkyl or aryl group, R^{19} is a hydrogen atom or an optionally substituted alkyl group and R^{20} is an optionally substituted alkyl group.

[0014] The use of beta-ketoamide groups in Michael donors for curing coating systems is mentioned in US-A-4871822, US-A-5084536 and EP-A-697444 but is not suggested as being particularly useful in conjunction with Michael acceptors which contain doubly activated olefinic groups. We have found that the combination of a Michael donor having beta-ketoamide groups with a Michael acceptor having doubly activated olefinic groups provides a coating composition curable at ambient temperature many times faster than known Michael curing coatings, for example about 100 or even 1000 times faster than similar coatings based on acetoacetate groups and acrylate groups.

[0015] The use of enamine carboxylate groups in Michael donors is mentioned in US-A-5426156 but is not suggested as being particularly useful in conjunction with Michael acceptors which contain doubly activated olefinic groups. We have found that the combination of a Michael donor having enamine beta-carboxylate groups with a Michael acceptor having doubly activated olefinic groups provides a coating composition which cures rapidly at ambient temperature without need for a basic catalyst.

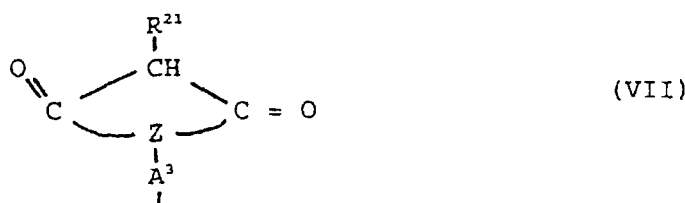
[0016] The coating, adhesive or sealant composition according to the present invention comprises (A) a Michael acceptor which is a compound or polymer containing at least two activated olefinic double bonds and (B) a Michael donor which is a compound or polymer containing at least two nucleophilic groups. The nucleophilic groups of the Michael donor (B) can be groups selected from:

(i) enamine amide groups of the formula:



where at least one of the groups R^{14} , R^{15} , R^{16} and R^{17} is an optionally substituted alkylene radical or one of the groups R^{14} , R^{15} and R^{16} is an optionally substituted arylene radical, whereby the enamine amide group is linked to the compound or polymer (B), and of the remaining groups R^{14} , R^{15} and R^{16} are hydrogen atoms or optionally substituted alkyl or aryl groups, provided that R^{14} and R^{15} are not both aryl or arylene groups, and R^{17} is a hydrogen atom or an optionally substituted alkyl group;

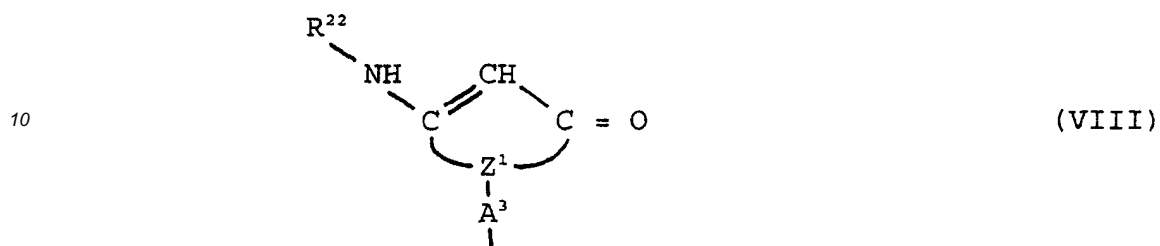
(ii) heterocyclic groups of the formula:



where R^{21} is a hydrogen atom or an optionally substituted alkyl group, Z is a trivalent radical completing a heterocyclic 5- to 7- membered ring and A^3 is a radical of valency at least 2 or a linking bond whereby the heterocyclic group is linked to the compound or polymer (B) ;

(iii) heterocyclic groups of the formula

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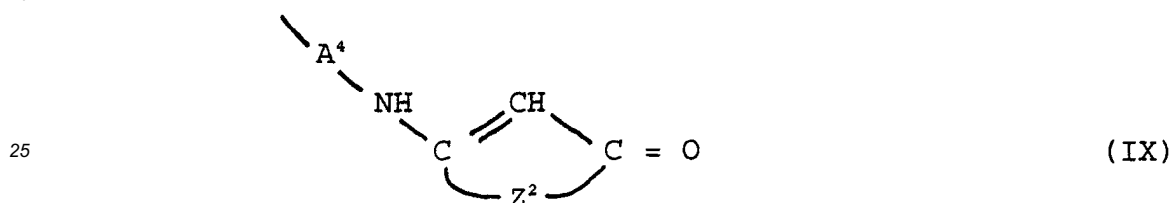


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where R^{22} is a hydrogen atom or an optionally substituted alkyl group, Z^1 is a trivalent radical completing a heterocyclic 5- to 7-membered ring and A^3 is defined as above;

(iv) heterocyclic groups of the formula

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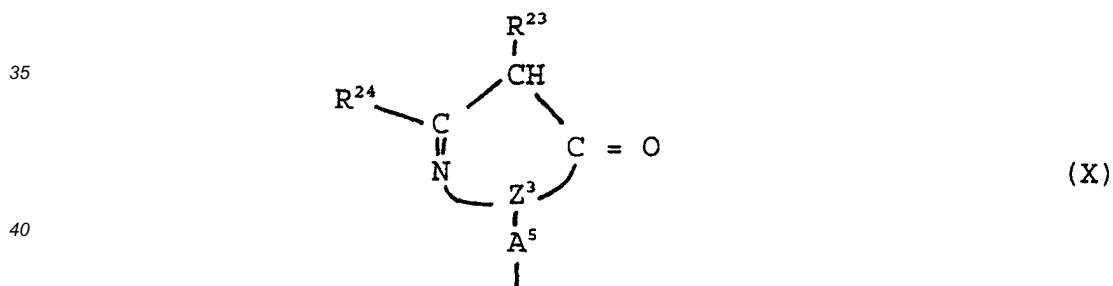


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where Z^2 is a divalent radical completing a heterocyclic 5- to 7-membered ring and A^4 is an optionally substituted alkylene radical whereby the heterocyclic group is linked to the compound or polymer (B) ;

(v) heterocyclic groups of the formula:

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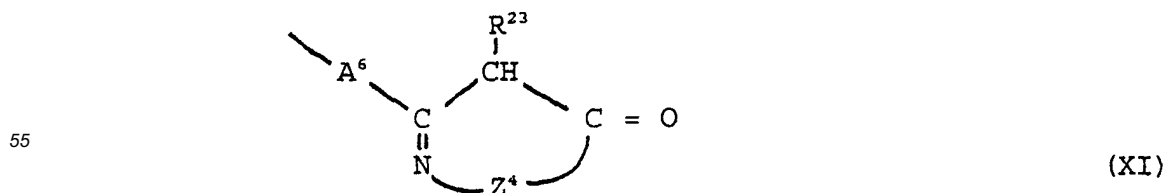


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where R^{23} is a hydrogen atom or an optionally substituted alkyl group; R^{24} is a hydrogen atom or an optionally substituted alkyl or aryl group; Z^3 is a trivalent radical completing a 5- to 7- membered heterocyclic ring and A^5 is a radical of valency at least 2 or a linking bond whereby the heterocyclic group is linked to the compound or polymer (B) ;

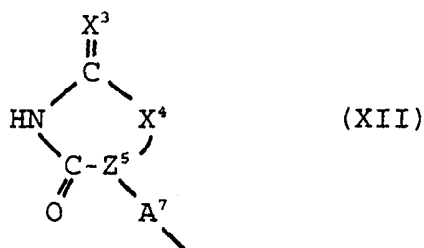
(vi) heterocyclic groups of the formula:

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where R²³ is a hydrogen atom or an optionally substituted alkyl group; Z⁴ is a divalent radical completing a 5- to 7- membered heterocyclic ring and A⁶ is an optionally substituted alkylene or arylene radical or a linking bond whereby the heterocyclic group is linked to the compound or polymer (B);
 (vii) heterocyclic groups of the formula:

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where X³ is an oxygen or sulphur atom; X⁴ is -O-, -S- or

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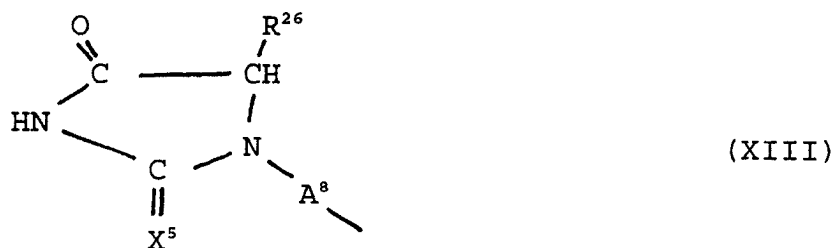


where R²⁵ is a hydrogen atom or an optionally substituted alkyl group; Z⁵ is a trivalent radical completing a 5- to 7- membered heterocyclic ring; and A⁷ is a radical of valency at least 2 or a linking bond whereby the heterocyclic group is linked to the compound or polymer (B);

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(viii) heterocyclic groups of the formula:

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where X⁵ is an oxygen or sulphur atom; R²⁶ is a hydrogen atom or an optionally substituted alkyl group; and A⁸ is an optionally substituted alkylene group whereby the heterocyclic group is linked to the compound or polymer (B);
 (ix) thio-containing ester or lactone groups of the formula:

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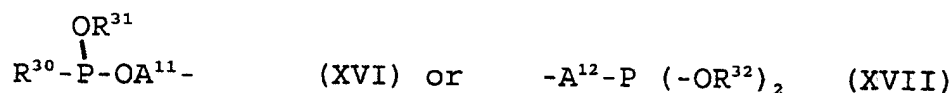


where R²⁷ is a hydrogen atom or an optionally substituted alkyl or aryl group and R²⁸ is an optionally substituted alkyl group or R²⁷ and R²⁸ together form an optionally substituted alkylene linkage completing a lactone ring and A⁹ is an optionally substituted alkylene or arylene group whereby the thio-containing ester or lactone group is linked to the compound or polymer (B), or R²⁹ is an optionally substituted alkyl or aryl group and A¹⁰ is an optionally substituted alkylene or arylene group whereby the thio- containing ester group is linked to the compound or polymer (B);

50

(x) phosphonite esters of the formula:

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5 where R³⁰ is an optionally substituted alkyl or aryl group, R³¹ is an optionally substituted alkyl group and A¹¹ is an optionally substituted alkylene group whereby the phosphonite ester group is linked to the compound or polymer (B) or R³¹ and A¹¹ are joined to form an optionally substituted alkylene linkage which completes a cyclic phosphonite ester ring, which alkylene linkage is substituted by a chemical linkage to the compound or polymer (B); A¹² is an optionally substituted alkylene or arylene group whereby the phosphonite ester group is linked to the compound or polymer (B) and the groups R³² are each optionally substituted alkyl groups which are the same or different or are joined to form a heterocyclic ring; and
 10 (xi) phosphinite esters of the formula:



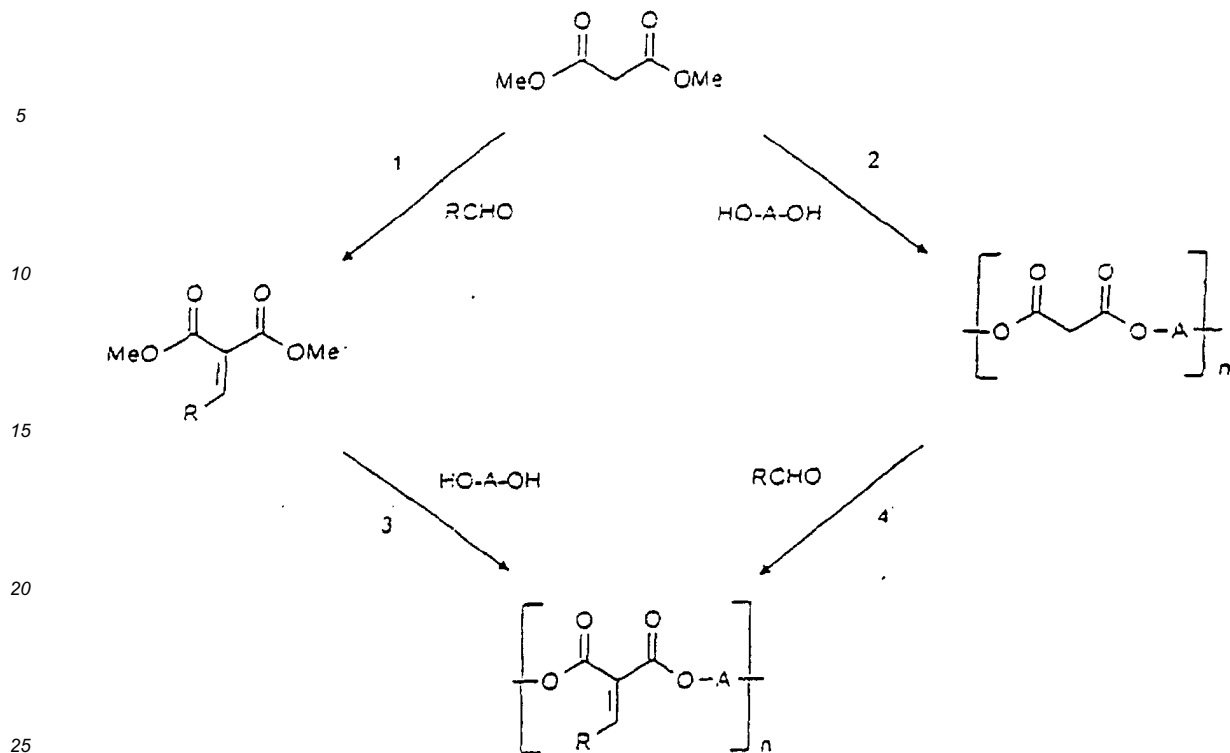
15 where each group R³³, which may be the same or different, is an optionally substituted alkyl or aryl group; A¹³ is an optionally substituted alkylene group whereby the phosphinite ester group is linked to the compound or polymer (B) or one of the groups R³³ and A¹³ are joined to form an optionally substituted alkylene linkage which completes a cyclic phosphinite ester ring, which alkylene linkage is substituted by a chemical linkage to the compound or polymer (B); A¹⁴ is an optionally substituted alkylene or arylene group whereby the phosphinite ester group is linked to the compound or polymer (B); R³⁴ is an optionally substituted alkyl group and R³⁵ is an optionally substituted alkyl or aryl group or R³⁴ and R³⁵ are joined to form a heterocyclic ring.
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30 **[0017]** We have found that Michael donors containing groups of any of the formulae (IV) to (XIX) are substantially more active in Michael curing coatings than are the acetoacetates described in US-A-4408018 and GB-A-2048913, the malonates described in US-A-4602061 or the amines described in US-A-4730033 and are capable of giving more rapid curing at ambient temperature and/or curing with less powerful alkaline catalysts. No base catalyst is required when using Michael donors containing thio-containing ester or lactone groups of formula (XIV) or (XV) or phosphonite or phosphinite esters of formulae (XVI) to (XIX).
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[0018] The polymer having repeating units of formula (I) can for example be a polyester in which the groups X and X¹ represent oxygen atoms or a polyamide in which the groups X and X¹ represent groups of the formula:



40 where R² is hydrogen or an alkyl group. Polyesters can for example be synthesised from a di(lower alkyl) malonate such as dimethyl malonate by either of two different routes, as illustrated in the following reaction scheme:
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in which Me=methyl, R is a monovalent aliphatic or aromatic group or hydrogen and A is a divalent aliphatic group.

[0019] The first route (1 and 3) uses the synthesis of dimethyl alkylidenemalonate from dimethyl malonate and an aldehyde RCHO by the Knoevenagel reaction (Reaction 1). Reaction 3 gives the polyester oligomer by a transesterification polymerisation reaction of the alkylidenemalonate with a diol HO-A-OH.

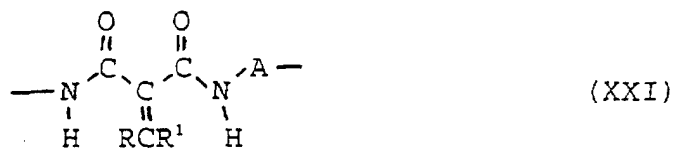
[0020] The second route (2 and 4) uses the synthesis of a malonate polyester oligomer from dimethyl malonate and a diol (Reaction 2). Reaction of the oligomer with an aldehyde by the Knoevenagel reaction produces the doubly activated double bond on each malonate site (Reaction 4). Malonyl di(acid chloride) can be used in place of the dialkyl malonate ester in Reaction 2.

[0021] The Knoevenagel reaction can for example be carried out by the use of Dean and Stark apparatus where the starting aldehyde and malonate compound are refluxed in toluene with a base catalyst such as piperidine or morpholine and an acid catalyst such as benzoic acid or acetic acid. Water, the reaction co-product, is separated and collected in the Dean and Stark graduated tube. An alternative procedure uses a titanium tetrachloride tetrahydrofuran complex and pyridine or N-methylmorpholine as the respective acid and base catalysts. This reaction is carried out under nitrogen at around 0°C with stirring. These lower temperature reaction conditions are preferred, especially for lower boiling aldehydes.

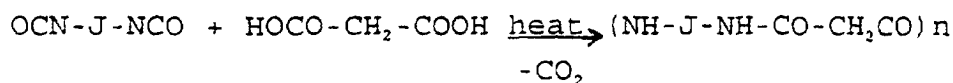
[0022] The transesterification reaction (Reactions 2 and 3) is carried out at temperatures of up to 190°C with vigorous stirring. A nitrogen purge can be used to facilitate distillation of the methanol condensate. A Dean and Stark apparatus can be used to collect the condensate, the amount of methanol collected being indicative of the progress of the reaction. n-Butyltin chloride dihydroxide or titanium tetraisopropoxide can be used as catalyst for the reaction. The degree of polymerisation of the polyester oligomer is dependent on the relative quantities of dimethyl malonate or dimethyl alkylidenemalonate and diol. For example, oligomers synthesised by using a mole ratio of 10:9 malonate to diol would at completion give a theoretical degree of polymerisation n of 9 and in practice give values of n of 6 to 9. Polymers having 3 to 20, particularly 5 to 10, activated C=C bonds and a molecular weight in the range 600 to 5000 are generally suitable as Michael acceptors in coating and sealant compositions according to the invention. For use in coatings, the reactive oligomer preferably has a low Tg (-30°C to -80°C) and a viscosity of less than 1.5 Pa s (15 poise).

[0023] Suitable aldehydes for use in the Knoevenagel reaction (1 or 4) are acetaldehyde (R=CH₃), formaldehyde (R=H), butyraldehyde (R=n-C₃H₇), isobutyraldehyde (R=i-C₃H₇), isovaleraldehyde (R=i-C₄H₉) and benzaldehyde (R=C₅H₅). The diol HO-A-OH is preferably a straight-chain alkanediol HO(CH₂)_mOH where m=2-10, for example propane-1,3-diol, butane-1,4-diol, hexane-1,6-diol or decane-1,10-diol, although branched diols such as propylene glycol or neopentyl glycol or ether-containing diols such as diethylene glycol can be used.

[0024] The polymer having repeating units of formula I can alternatively be a polyamide. For example, a polyamide having repeating units of the formula:

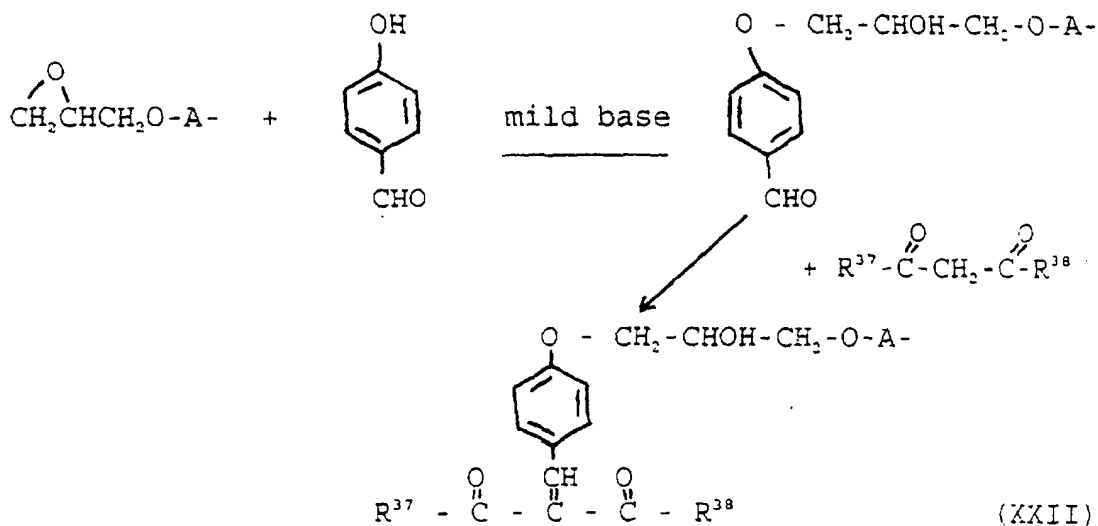


can be prepared by reaction of a di(lower alkyl) malonate or malonyl di(acid chloride) with a di(primary amine) H₂NANH₂ to form a polyamide followed by Knoevenagel reaction with an aldehyde RCHO or ketone RCOR¹. Alternatively, a diisocyanate OCN-J-NCO can be heated with malonic acid to form a polyamide

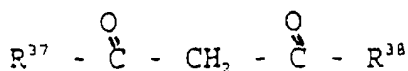


which can undergo a Knoevenagel reaction to introduce the activated C=C bond. In the latter reaction, the steps can be carried out in reverse order, that is malonic acid can be reacted with an aldehyde or ketone in a Knoevenagel reaction and the resulting unsaturated dicarboxylic acid can be heated with a diisocyanate to produce a polyamide. Polyamides possess considerable hydrolytic stability, as well as good resistance to other substances such as hydraulic fluid. Advantage may also be taken of the affinity of amides for water; water can be used as a solvent, diluent or plasticiser in coating or adhesive compositions based on a polyamide having repeating units of formula XXI.

[0025] The compound or polymer containing at least two doubly activated olefinic groups of formula (II) can be prepared from a compound containing at least two glycidyl groups, such as the diglycidyl ether of bisphenol A or a glycidyl acrylate polymer, by reaction with a hydroxy-substituted aldehyde such as p-hydroxybenzaldehyde, which can optionally be further substituted, for example 4-hydroxy-3-methoxybenzaldehyde, followed by Knoevenagel reaction with a beta-dicarbonyl compound, preferably a beta-diketone, as shown in the following reaction scheme:-



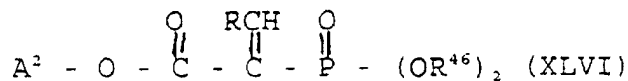
The beta-diketone



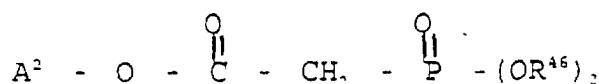
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can for example be benzoylacetone, alpha-thenoyltrifluoroacetyl methane, pivaloyl propionyl methane or bis(alpha-furo-yl)methane. The resulting compound of formula (XXII) contains no ester linkages and is extremely resistant to hydrolysis.

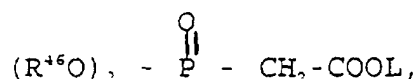
[0026] The Michael acceptor of formula (XLV) containing at least two doubly activated olefinic groups can for example be a phosphonocarboxylate ester containing groups of the formula



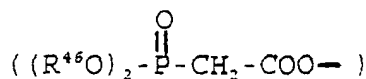
where A²- is the residue of a polyol A²-(OH)_n. Such a Michael acceptor can be prepared by reacting the chloroacetate of a polyol, for example butane-1,4-diol bis(chloroacetate), with trialkyl phosphite to form the phosphonoacetate



of the polyol, and then carrying out a Knoevenagel reaction with an aldehyde RCHO under the conditions described above. The compound or polymer of formula (XLVI) can alternatively be prepared by a transesterification reaction of a phosphonocarboxylate triester of the formula

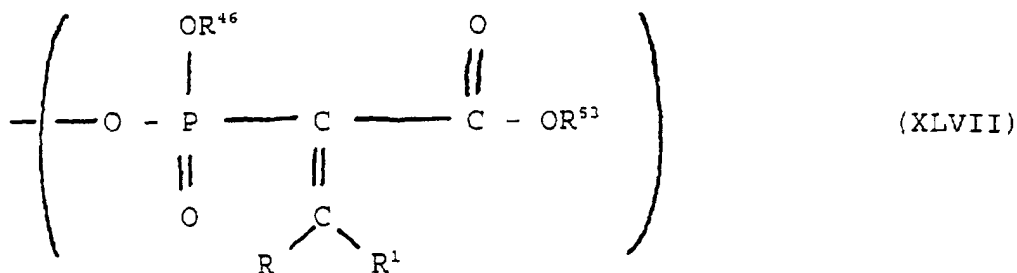


where L is a lower alkyl group, for example a methyl or ethyl group, with a polyol such as 1,6-hexanediol or trimethylolpropane to prepare a polyol ester containing at least two

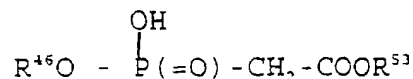


groups, followed by a Knoevenagel reaction. Alternatively the phosphonocarboxylate triester can be reacted first with an aldehyde in a Knoevenagel reaction followed by transesterification with a polyol.

[0027] The compound or polymer of formula (XLV) can alternatively contain at least two groups of the formula

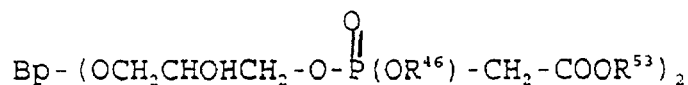


where R⁵³ is an alkyl or aryl group which is optionally substituted. Such a polymer can for example be prepared by reaction of an acidic phosphonocarboxylate diester of the formula



with a compound or polymer containing at least two glycidyl groups, for example the diglycidyl ether of bisphenol A or hydrogenated bisphenol A, to prepare a polyol ester such as

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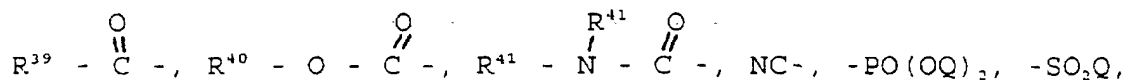
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where Bp is a bisphenol A nucleus. This polyol ester can undergo a Knoevenagel reaction with an aldehyde RCHO to form a compound or polymer containing at least two groups (XLVII).

15

[0028] The polymer having repeating units of formula (I) or containing groups of formula (II) can for example be used in a coating, adhesive or sealant composition with a Michael donor in which the nucleophilic groups are thiol groups, for example 1,6-hexanedithiol, bis(2-mercaptoethyl)ether or pentaerythritol tetrakis (beta-mercaptopropionate), primary or secondary amine groups, for example diethylene triamine or an amine-tipped polyether, phosphite ester groups or active hydrogen groups of the formula Y-CH-Y¹, where Y and Y¹ are each selected from groups of the formula:

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pyridyl or triazinyl, R³⁹, R⁴⁰ and Q each represent an alkyl or aryl group and each group R⁴¹ represents a hydrogen atom or an alkyl group. The Michael donor can for example be a material containing at least two acetoacetate groups, cyanoacetate groups or beta-diketone groups, for example a polymer of acetoacetoxyethyl methacrylate or trimethylolpropane tris(acetoacetate). The polymer having repeating units of formula (I) can alternatively be used with a Michael donor containing groups having any of the formulae (IV) to (XIX).

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[0029] The beta-ketoamide groups of formula (IV) can be prepared by the reaction of primary or secondary amine groups with diketene as described in US-A-4871822 or with tetrahydropyrantrione (acetone dicarboxylic anhydride) as described in J. Chem. Soc. C 1971 at p.2721 or by the reaction of amine groups with a cyclic acetone diketene adduct. A polyamine such as diethylene triamine or an amine-tipped polyether can for example be reacted with diketene or tetrahydropyrantrione to prepare a material containing at least two beta-ketoamide groups.

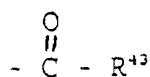
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[0030] The enamine beta-carboxylate groups of formula (VI) can be formed by the reaction of beta-ketoesters such as acetoacetates with amines or ammonia at ambient or slightly elevated temperatures of up to 100°C, particularly 20-100°C. Higher temperature reaction of beta-ketoesters with amines or ammonia, for example at about 180°C, forms beta-ketoamides. In general, a poly(acetoacetate) can be reacted with ammonia, or a monoamine or a polyamine can be reacted with an alkyl acetoacetate, to produce materials containing two or more enamine beta-carboxylate groups of formula (VI). The enamine beta-carboxylate groups need not be preformed. A compound containing at least two beta-ketoester groups, for example trimethylolpropane tris(acetoacetate), and a substantially non-volatile primary amine having at least 6 carbon atoms can be mixed to form a component of the coating composition. They will react at least partially to form enamine beta-carboxylate groups and will react further as the enamine beta-carboxylate groups are consumed in the Michael curing reaction. The enamine beta-carboxylate groups of formula (VI) can alternatively be formed by the reaction of an amine, for example a polyamine such as a di(primary amine), with an acetylenecarboxylate ester.

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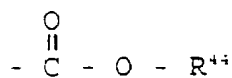
[0031] The material containing at least two beta-ketoamide groups, or the material containing at least two enamine beta-carboxylate groups, is used in a Michael curing coating, adhesive or sealant composition with a Michael acceptor which is a compound or polymer containing at least two doubly activated olefinic groups. The Michael acceptor can for example be a polymer containing repeating units of formula (I) or a compound or polymer containing at least two groups of formula (II) or (XLV). The electron-withdrawing groups of the Michael acceptor are preferably selected from -CN, acyl groups of the formula

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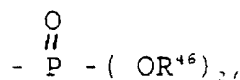
where R⁴³ is an optionally substituted alkyl or aryl group, ester groups of the formula



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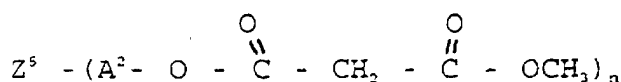
where R⁴⁴ is an optionally substituted alkyl or aryl group, amide groups of the formula -CON(R⁴⁵)₂ where each group R⁴⁵, which can be the same or different, is selected from hydrogen and optionally substituted alkyl or aryl, or a triazine group which is optionally substituted, a phosphonate ester group of the formula

5



10 where R⁴⁶ is an optionally substituted alkyl or aryl group, a sulphone group of the formula -SO₂R⁴⁷, where R⁴⁷ is optionally substituted alkyl or aryl, or an alpha- or gamma-pyridyl group. The Michael acceptor can for example be prepared from a polyhydroxy compound Z⁶-(A²OH)_n where Z⁶ is a core radical of functionality (n) at least 2 and A² is an optionally substituted alkylene group, by reaction with either an alkyl malonate diester such as dimethyl malonate to produce the poly (methyl malonate) ester

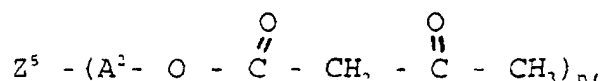
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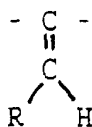
or diketene or a diketene adduct to produce the poly(acetoacetate) ester

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followed in either case by a Knoevenagel reaction with an aldehyde RCHO to convert the active methylene group to a

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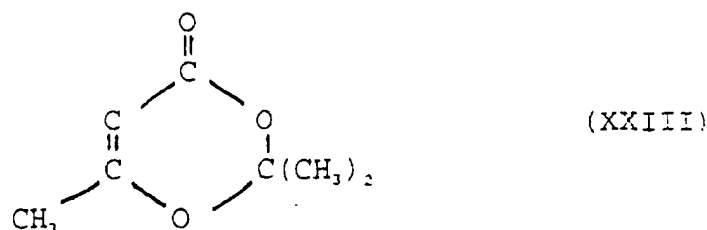
linkage. The polyhydroxyl compound can for example be trimethylolpropane, pentaerythritol or the oligomer octa-caprolactone tetrol sold under the Trade Mark CAPA 316 and having equivalent weight 262 g/mol and Tg -66°C.

40

[0032] A dialkyl malonate such as dimethyl malonate can be reacted with a polyhydroxyl oligomer in a transesterification reaction at about one mole dimethyl malonate per hydroxyl group of the oligomer at temperatures of up to 180°C with stirring. An organometallic compound such as butyltin chloride dihydroxide is generally used as a catalyst for the reaction. The progress of the reaction can be followed by the amount of methanol co-product evolved.

[0033] The acetoacetylation reaction can be carried out using diketene or a cyclic diketene/acetone adduct such as 2,2,6-trimethyl-4H-1,3-dioxin-4-one.

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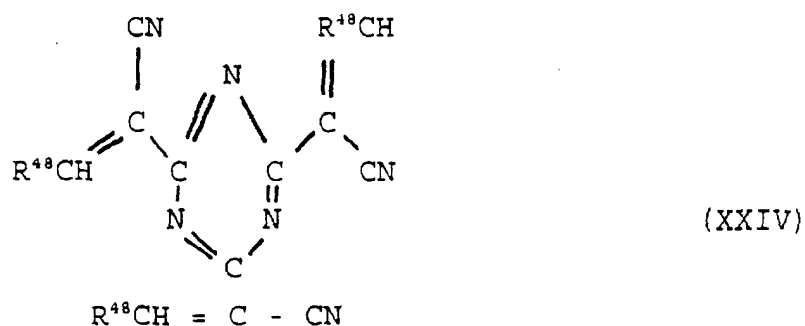
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[0034] This compound decomposes when heated above 100°C, for example at 120-180°C, to provide acetylketene and acetone and readily reacts with hydroxyl groups by acetoacetylation.

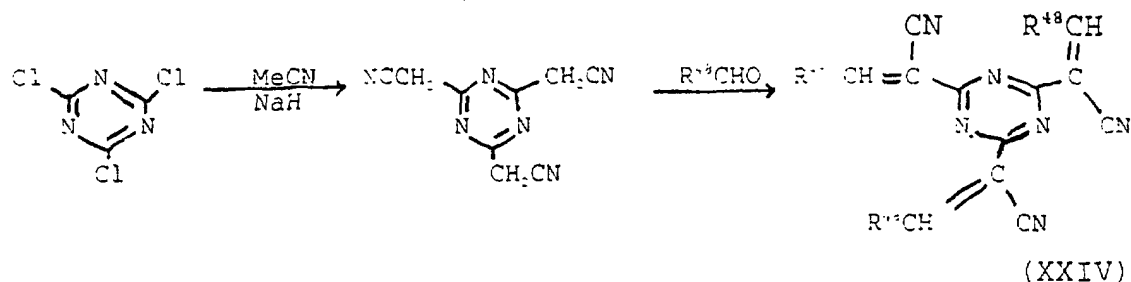
[0035] The subsequent Knoevenagel reaction can be carried out under the conditions and using the aldehydes as

described above, most preferably at 0°C using titanium tetrachloride tetrahydrofuran complex and pyridine as the respective acid and base catalysts.

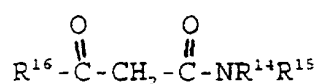
[0036] The Michael acceptor containing at least two doubly activated olefinic groups can alternatively be a triazine compound of the formula:



where R⁴⁸ is hydrogen or an alkyl or aryl group. Such a triazine compound can be prepared from cyanuric chloride by the following reaction scheme:

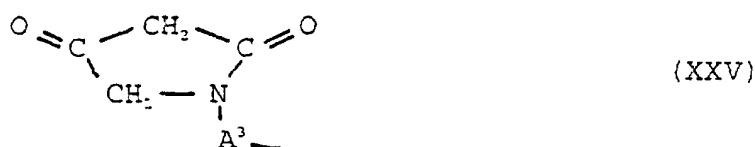


[0037] The enamine amide groups of formula (V) can be formed by the reaction of beta-ketoamide groups with primary amine groups. For example, a polyamine of the formula Z⁷ - (R¹⁷NH₂)_n, where Z⁷ is a core radical of valency n, for example a diamine such as hexamethylene diamine, can be reacted with a beta-ketoamide of the formula



under the conditions described in US-A-4089845 and US-A-1161580. Alternatively, a compound or polymer containing beta-ketoamide groups, prepared as described above, can be reacted with an amine of the formula R¹⁷NH₂.

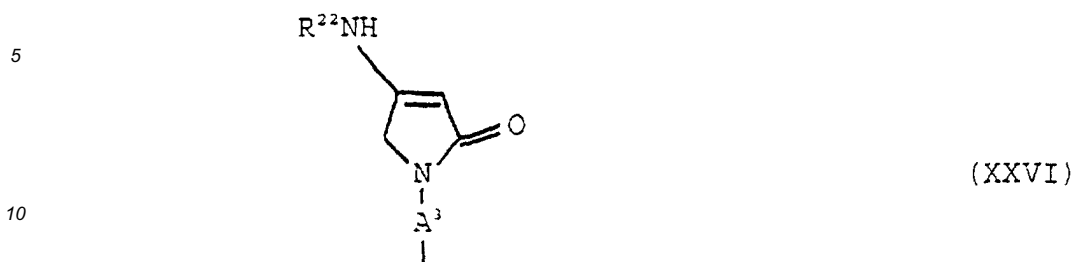
[0038] The heterocyclic groups of formula (VII) can for example be cyclic beta-ketocarboxylic amide groups such as pyrrolidindione groups of the formula:



[0039] These can be formed by the reaction of an amine, for example a polyamine of the formula A³(NH₂)_n such as hexamethylene diamine, with 2,2-dimethyl-6-bromomethyl-1,3-dioxen-4-one (the bromination product of (XXIII)) with elimination of acetone.

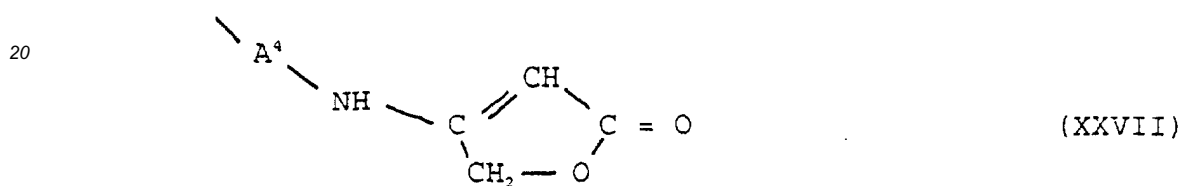
[0040] The heterocyclic groups of formula (VIII) can for example be amino-substituted pyrrolinone groups of the

formula:

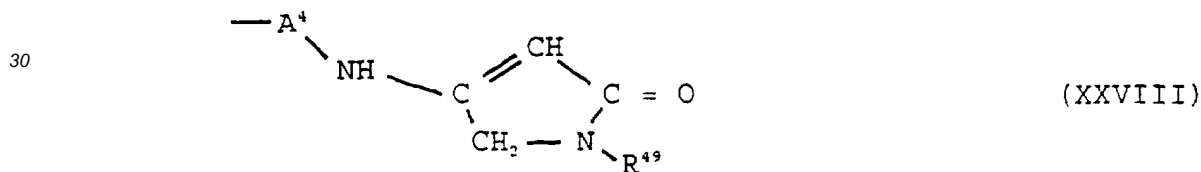


which can be formed from pyrrolidindione groups of formula (XXV) by reaction with an amine $R^{22}NH_2$.

15 **[0041]** The heterocyclic groups of formula (IX) can for example be cyclic enamine beta-carboxylate ester groups such as 4-aminofuranone groups of the formula:-

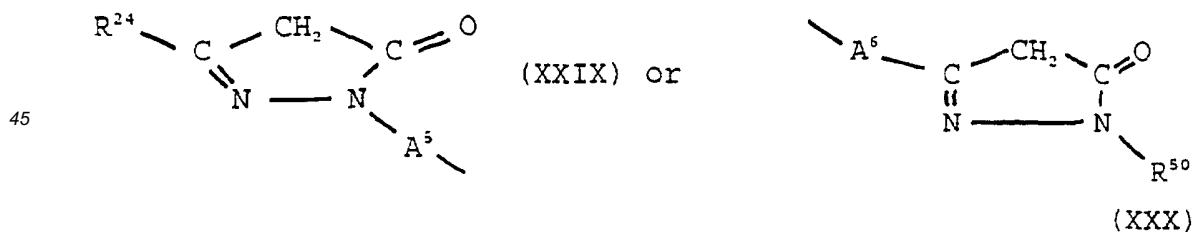


or cyclic enamine beta-carboxylic amide groups such as 4-aminopyrrolinone groups of the formula



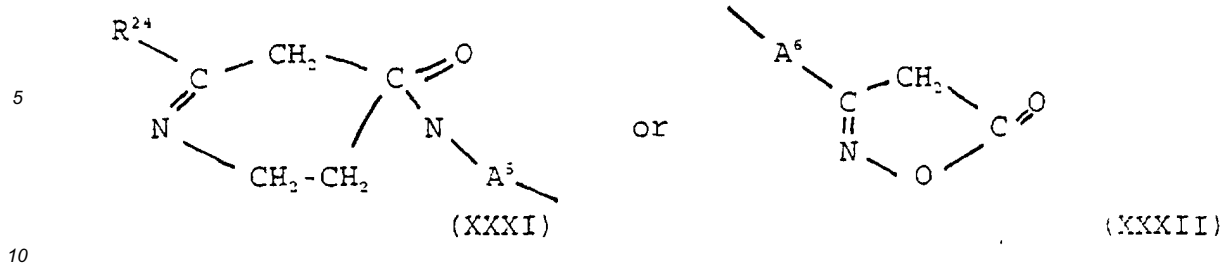
where R^{49} is hydrogen or an alkyl or aryl group. The 4-aminofuranone groups of formula (XXVII) can for example be prepared by reaction of a polyamine $A^4(NH_2)_n$ with furan-2,4-dione or a gamma-chloroacetoacetate ester. The 4-aminopyrrolinone groups of formula (XXVIII) can be prepared by reacting a polyamine $A^4(NH_2)_n$ with a pyrrolidindione.

[0042] The heterocyclic groups of formula (X) or (XI) can for example be pyrazolone groups of the formula:



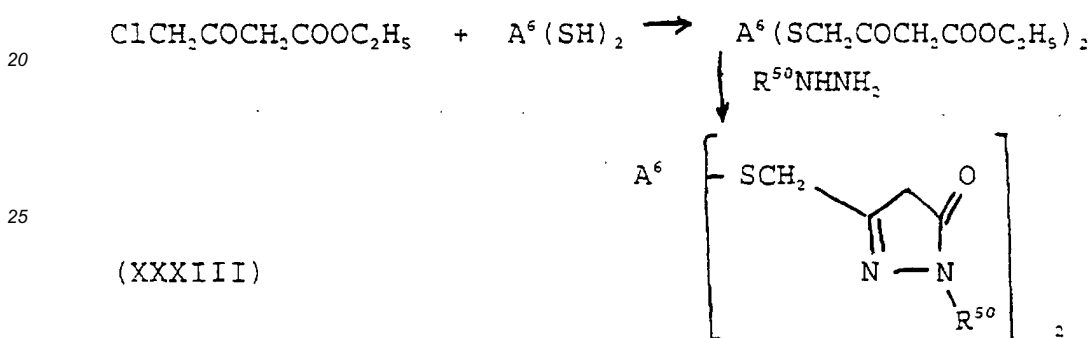
where R^{50} is a hydrogen atom or an alkyl or aryl group, or tetrahydro-1,4-diazepin-5-ones of the formula (XXXI) or isoxazolones of the formula (XXXII)

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The pyrazolone groups can readily be synthesised by reaction of hydrazines with beta-ketoester groups. Pyrazolones of formula (XXIX) can be formed from poly(hydrazines), particularly bishydrazines of the formula $A^5(NHNH_2)_2$, by reaction with a beta-ketoester such as methyl or ethyl acetoacetate. Pyrazolones of formula (XXX) can be formed by reaction of a big(4-thioacetoacetate), formed from a dithiol and a gamma-chloroacetoacetate, with hydrazine or an alkylhydrazine or arylhydrazine.

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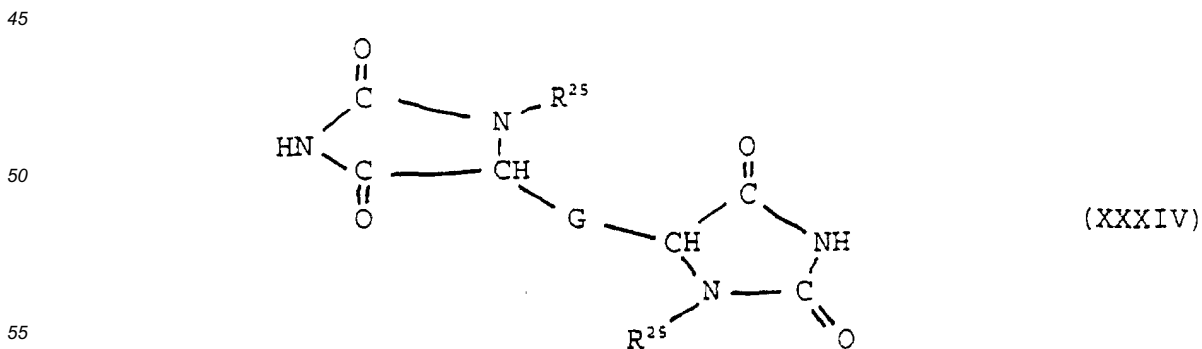
The tetrahydro-1,4-diazepin-5-ones can likewise be synthesised from 1,2-diamines by reaction with a beta-ketoester as described for example in US-A-4315860. In particular, tetrahydrodiazepinones of formula (XXXI) can be synthesised by reaction of bis(beta-aminoamines) of the formula $A^5(NHCH_2CH_2NH_2)_2$ with methyl or ethyl acetoacetate or benzoylacetate. Isoxazolone groups can be formed from beta-ketoester groups by reaction with hydroxylamine.

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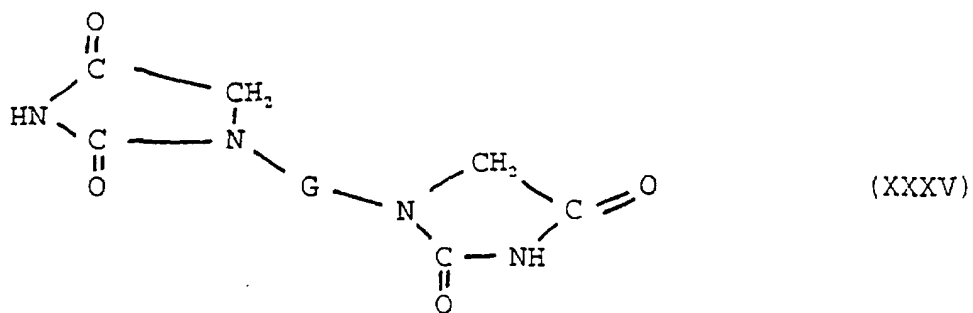
[0043] The heterocyclic groups of formula (XII) or (XIII) can for example be hydantoinis where X^3 or X^5 is O, and Z^5 is $>CH-$ with X^4 being



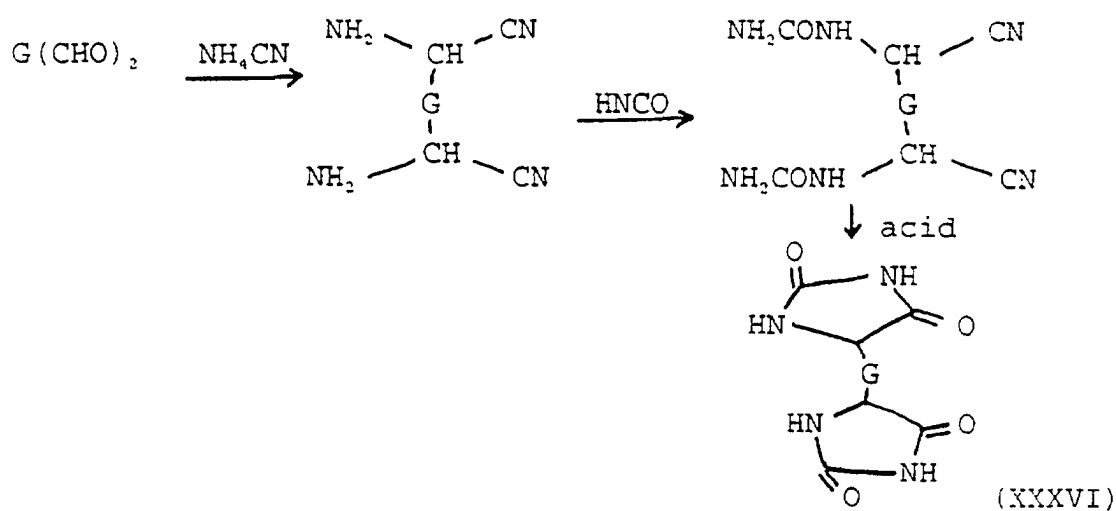
for example compounds having groups of formula (XII) can be bis(hydantoinis) of the formula:

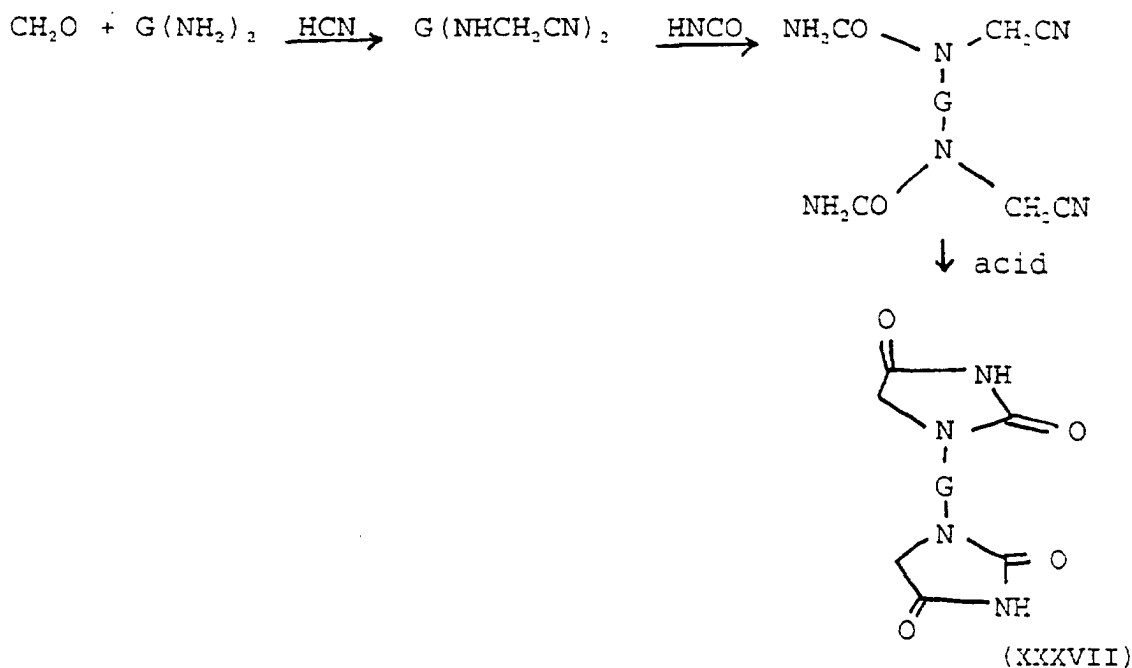


or compounds having groups of formula (XIII) can be bis(hydantoins) of the formula:

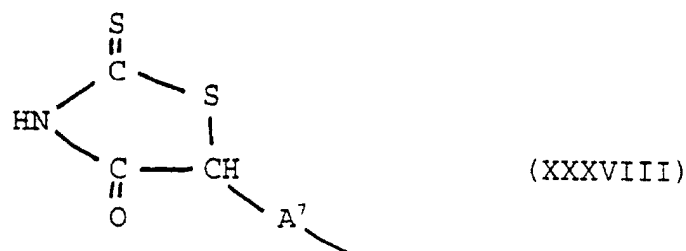


15 where G is a hydrocarbon or polyether chain. Compounds of formula (XXXIV) can be prepared from a hydrocarbon or polyether chain tipped with aldehyde groups, and compounds of formula (XXXV) can be prepared from a hydrocarbon or polyether chain tipped with primary amine groups, as shown by the following reaction schemes:-



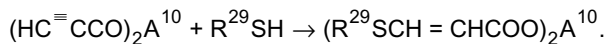


25 Alternatively, the heterocyclic groups of formula (XII) or (XIII) can be analogous 2-thiohydantoin groups in which X³ or X⁵ is a sulphur atom; these can be prepared by reactions similar to the above using HSCN in place of HNCO. As a further alternative, the heterocyclic groups of formula (XII) can be rhodanine groups of the formula:

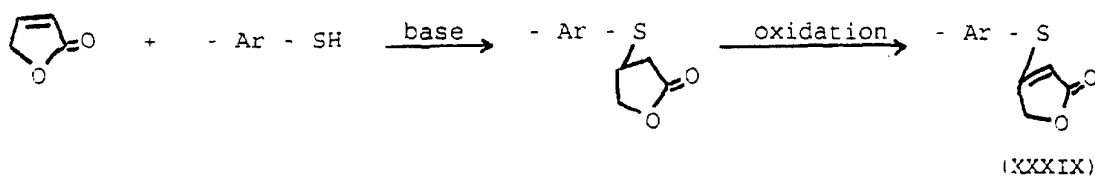


40 Compounds containing rhodanine groups of formula (XXXVIII) can be prepared from a hydrocarbon or polyether chain tipped with alpha-halo (chloro or bromo)-carboxylic acid groups by reaction with ammonium dithiocarbamate.

[0044] Thio-containing unsaturated ester groups of formula (XV) can be formed from a mercaptan and the diester of a diol and an alkynylcarboxylic acid

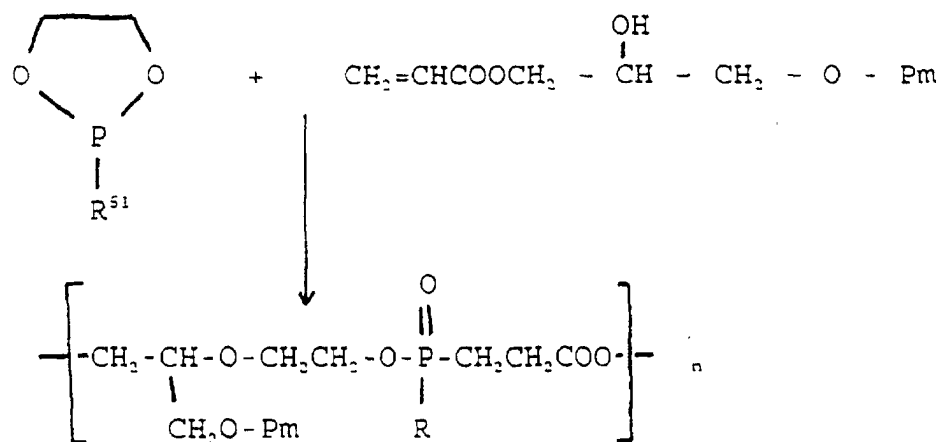


Thio-containing lactone groups of formula (XIV) can be formed by Michael addition of a bis-mercaptan and a butenolide, followed by oxidation to regenerate the butenolide ring



where Ar is an arylene group.

[0045] The phosphonite ester groups (XVI) or (XVII) or phosphinite ester groups (XVIII) or (XIX) can for example be formed by reaction of a compound or polymer containing free hydroxyl groups with the appropriate organophosphorus chloride. If a cyclic phosphonite ester or phosphinite ester is used, the compound or polymer (B) need only contain one such cyclic phosphonite or phosphinite ester group, since this will react both by Michael-type addition and by ring-opening polymerisation of the Michael adduct to form a crosslinked network. For example, a cyclic phosphonite ester will react with an acrylate-functional polymer containing acrylate groups derived from the reaction of glycidyl groups with acrylic acid as shown below



where Pm is a polymer residue. Other compounds or polymers containing at least two activated olefinic double bonds such as acrylate groups can be used. The invention therefore includes a coating, adhesive or sealant composition curable by Michael reaction comprising (A) a Michael acceptor which is a compound or polymer containing at least two activated olefinic double bonds and (B) a Michael donor which is a compound containing a nucleophilic group, characterised in that the nucleophilic group of the Michael donor (B) is selected from cyclic phosphonite esters of the formula:-



and cyclic phosphinite esters of the formula:



where R⁵¹ and R⁵² each represent an optionally substituted alkyl or aryl group and A¹⁶ and A¹⁷ each represent an optionally substituted alkylene group. The alkylene group A¹⁶ preferably contains 2 to 4 carbon atoms, for example the cyclic phosphonite ester can be ethylene phenylphosphonite, which is readily prepared from C₆H₅PCl₂ and ethylene glycol. Cyclic phosphonite ester groups can in general be readily prepared by hydrolysis of epoxide groups. Particularly preferred Michael donors are those containing two or more cyclic phosphonite ester groups (compounds of formula (XVI) in which R³¹ and A¹¹ are joined) derived from polyepoxides such as the diglycidyl ether of bisphenol A, a glycidyl acrylate polymer or the diepoxide of 1,7-octadiene. The alkylene group A¹⁷ preferably contains 3 to 5 carbon atoms.

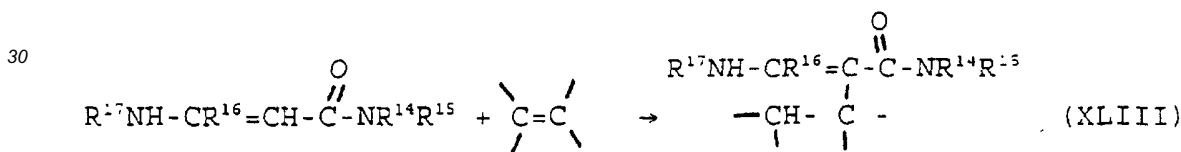
[0046] The Michael donor compounds containing nucleophilic groups of any of the formulae (V) to (XIX) can in general

be used in coating, adhesive or sealant compositions with any Michael acceptor containing at least two activated olefinic double bonds according to the present invention. The Michael acceptor contains doubly activated olefinic double bonds, for example a polymer containing repeating units of formula (I) or a polymer or compound containing groups of formula (II), (III) or (XLV), for most rapid curing.

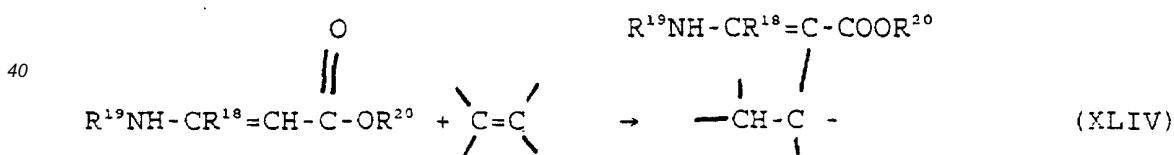
5 [0047] Many of the coating, adhesive or sealant compositions of the invention preferably contain a basic catalyst, although Michael donors of formulae (XIV) to (XIX) cure readily without the use of basic catalysts. Tertiary amine catalysts are usually preferred as basic catalysts. These may be strongly basic amines such as diazabicycloundecene or diazabicyclononene or a substituted guanidine for most rapid curing or less basic tertiary amines such as triethylamine. US-A-4408018 teaches that tertiary amines such as triethylamine are not sufficiently alkaline to act as catalysts for Michael curing coating compositions, but we have found that compositions containing a Michael donor having nucleophilic groups of formula (IV) or any of formulae (VII) to (XIII) can cure in less than an hour at ambient temperature when catalysed by triethylamine, particularly if the Michael acceptor contains doubly activated olefinic double bonds. In one preferred embodiment of the invention, a tertiary amine capable of imparting stability against degradation by light, particularly UV light and sunlight, is used as catalyst, preferably as the only basic catalyst. Such an amine is generally a sterically hindered amine such as pentamethylpiperidine or a derivative thereof, particularly bis (1,2,2,6,6-pentamethyl-4-piperidyl) sebacate sold commercially under the Trade Mark Tinuvin 292.

15 [0048] An alternative form of preferred catalyst is an alkali metal salt of an activated methylene compound in which the methylene is activated by two adjacent electron-withdrawing groups, for example the sodium or potassium salt of an acetoacetic ester such as ethyl acetoacetate or a malonate diester such as diethyl malonate.

20 [0049] Michael donor compounds containing enamine amide groups of formula (V), enamine beta-carboxylate groups of formula (VI), cyclic enamine amides or beta-carboxylates of formula (VIII) or (IX) or thio-containing ester or lactone groups of formula (XIV) or (XV) have the advantage that they can form coating compositions with Michael acceptors which will cure at ambient temperature without the need for any catalysts, for example in a time of 2 to 3 hours when a Michael acceptor containing doubly activated olefinic double bonds is used. The point of nucleophilic reaction, in contradistinction to other amines which take part in a Michael-type reaction, is not through the N atom. For example, a group of formula (V) reacts with an activated double bond as follows:



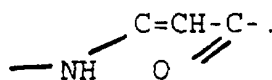
35 and a group of formula (VI) reacts as follows:



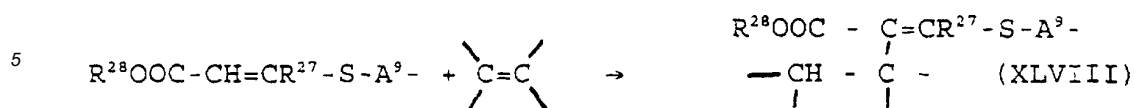
45 In general, the nucleophilic groups (IV) to (XIII) take part in the Michael reaction through an activated methylene group, for example in a linkage



55 this linkage alternatively may be represented



[0050] The groups of formulae (XIV) and (XV) react with an activated double bond as follows:



[0051] A Michael donor containing phosphonite or phosphinite ester groups, for example those of formulae (XVI) to (XIX), can be used with the same Michael acceptors described above, but the composition is preferably catalysed by a quaternary ammonium halide such as tetrabutylammonium iodide.

[0052] The compositions of the invention may contain an organic solvent, for example an aromatic hydrocarbon such as xylene, a ketone such as methyl isobutyl ketone or an ester or etherester such as butyl acetate or methoxypropyl acetate, or they may be solventless. Many of the Michael donors of formulae (IV) to (XIX) are liquids suitable for inclusion in solventless compositions or can be used with liquid Michael acceptors. Similarly, many of the Michael acceptors of formulae (I) to (III) or (XLV) are liquids or can be used with liquid Michael donors. Michael donors of asymmetric molecular structure may be preferred since they are more likely to be liquid or of low Tg and may give rise to tougher cured films.

[0053] The compositions of the invention are generally packaged as 2-pack compositions in which the Michael acceptor and the Michael donor are packaged separately and mixed up to 8 hours, preferably up to 2 hours, before use or at the time of application as in the case of coatings applied by twin-feed spray or sealants or adhesives applied from a twin-barrel applicator.

[0054] The coating, sealant or adhesive composition may contain additional ingredients. For example, coating compositions will generally contain pigments, for example anticorrosive pigments such as zinc phosphate or sodium zinc molybdate, or colouring and opacifying pigments such as titania, iron oxide or phthalocyanine pigments. Sealant compositions will also generally contain pigments and/or fillers such as calcium carbonate or talc and all types of composition may contain additives such as plasticisers, thixotropes such as silica gel or bentonite clay, or stabilising agents.

[0055] The invention is illustrated by the following Examples:-

Example 1

Poly-(1,6-hexanediol 1,1-propylenedicarboxylate)

[0056] A stirred mixture of dimethyl 1,1-propylenedicarboxylate (16.28g, 0.103 mol), 1,6-hexanediol (10.96g, 0.093 mol), n-butyltin chloride dihydroxide (0.53g) and p-quinol (1.74g) was heated under nitrogen to 130°C over 80 min and then to a maximum of 190°C over a further 100 min, with collection of methanol (7ml, 93%) in a Dean and Stark apparatus by distillation from the reaction mixture.

[0057] The cooled product (23.15g) was dissolved in dichloromethane, and the solution was washed with aqueous potassium sodium tartrate solution and dried (MgSO₄). Removal of solvent and drying (85°C/100 Pa/1hr) gave poly-(1,6-hexanediol 1,1-propylenedicarboxylate) as a viscous liquid (20.21g, yield 94%), identified by NMR. The polymer had olefinic functionality 7.9 and equivalent weight 253.

[0058] 1.51g polymer was mixed with 0.74g pentaerythritol tetrakis (β-mercaptoacrylate), cast as a film and cured at 95°C for 3 hours.

[0059] The crosslinked polymer film had: Tg -11°C by DSC, Tg -7°C by DMA, sol content 2%, linear swell (ethyl acetate) 19%, hydrolytic weight loss (1M NaOH, 1 week) 3%, initial 20° gloss 70, gloss retention 70% after 300 MJm⁻² solar UV exposure.

Examples 2 and 3

[0060] Following the procedure of Example 1, coating films were prepared from the polymer of Example 1 with bis(β-mercaptoethyl) ether (Example 2) or 1,6-hexanedithiol (Example 3). The results are shown in Table 1 below.

Table 1

	Example 2	Example 3
Weight of polymer of Example 1	1.56g	1.54g

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Table 1 (continued)

	Example 2	Example 3
Weight of bis (β -mercaptoethyl ether)	0.44g	-
Weight of 1,6-hexanedithiol	-	0.46g
Tg of cured film by DSC	-36°C	-36°C
Tg of cured film by DMA	-23°C	-21°C
Gloss retention after 300 MJm ⁻² UV	60%	75%

Example 4

Poly-(1,3-propanediol malonate)

[0061] A stirred mixture of dimethyl malonate (27.18g, 0.206 mol), 1,3-propanediol (14.05g, 0.185 mol) and titanium tetraisopropoxide (0.35g) was heated to 120°C over 30 min and then to a maximum of 170°C over a further 2.5 h, with collection of methanol (14 ml, 94%) in a Dean and Stark apparatus by distillation from the reaction mixture.

[0062] The cooled product (28.34g, 97%) was dissolved in dichloromethane, and the solution was washed with aqueous disodium hydrogen phosphate solution and dried (MgSO₄). Removal of solvent and drying (85°C/200 Pa/2h) gave poly-(1,3-propanediol malonate) as a viscous liquid (26.30g, yield 90%), identified by NMR. Degree of polymerisation 6.3; Molecular weight (Mn) 1040; Malonate equivalent weight 142.

Poly-(1,3-propanediol β,β -styrenedicarboxylate)

[0063] A solution of titanium tetrachloride in dichloromethane (1.0 M, 100 ml, 0.10 mol) was added slowly to tetrahydrofuran (200 ml) at 0-10°C, with stirring under nitrogen, to give a yellow precipitate of the TiCl₄/THF complex. To the stirred suspension of TiCl₄/THF (0.10 mol) in tetrahydrofuran/dichloromethane at 0-10°C was slowly added dropwise a solution of poly-(1,3-propanediol malonate) (7.55g, 0.0530 g eq wt) and benzaldehyde (6.41g, 0.0604 mol) in THF (30 ml). After 1.5 hours at 0°C, pyridine (15.65g, 0.20 mol) in THF (20 ml) was added dropwise at 0-10°C over 40 min, with separation of a brown gum. Stirring was continued for 20 hours at 0°C, during which the gum redissolved. Water and diethyl ether were then added to the light tan reaction mixture, the aqueous layer was washed with diethyl ether, and the combined organic phases were dried (MgSO₄). Removal of solvent and drying (100°C/100 Pa) gave poly-(1,3-propanediol β,β -styrenedicarboxylate) as a viscous liquid which on cooling became a gum (11.16g, yield 96%), identified by NMR. Degree of polymerisation 6.2; functionalisation of reactive sites 93%; Olefinic functionality 6.4; Molecular weight (Mn) 1550; Olefin equivalent weight 249.

[0064] 1.81g polymer (7.30 x 10⁻³ equivalents) was mixed with 0.91g (1.86 x 10⁻³ mol) pentaerythritol tetrakis (β -mercapropionate) (PETMP), 9.7 mg tri-n-butylamine and 0.14g toluene and allowed to cure at ambient temperature. Gelation occurred after 30 minutes. The crosslinked polymer film had: Tg 42°C (Tg[∞] 48°C) by DSC, initial 20° gloss 70, gloss retention 70% after 300 MJm⁻² solar UV exposure.

[0065] The curing reaction was repeated using 1.62g polymer, 0.70g PETMP, 9.6mg tri-n-butylamine and 0.55g di-n-butyl phthalate plasticiser. The cured film had Tg -2°C by DSC (+29°C by DMA), linear swell (ethyl acetate) 10%, and anhydrolytic weight loss (1M NaOH, 1 week) 2%,

Examples 5 and 6

[0066] Following the procedure of Example 4 coating films were prepared from the polymer of Example 4 and bis(β -mercaptoethyl) ether (Example 5) or 1,6-hexanedithiol (Example 6). The results are shown in Table 2 below.

Table 2

	Example 5	Example 6
Weight of polymer of Example 4	2.06g	2.06g
Weight of bis(β -mercaptoethyl)ether	0.48g	-
Weight of 1,6-hexanedithiol	-	0.51g
weight of tri-n-butylamine catalyst	14.1mg	26.6mg
Weight of di-n-butyl phthalate plasticiser	0.28g	0.28g

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Table 2 (continued)

	Example 5	Example 6
Tg of cured film by DSC	6°C	2°C
Tg of cured film by DMA	25°C	19°C
Linear swell (ethyl acetate)	17%	19%
Hydrolytic weight loss (1M NaOH, 1 week)	1%	0%
Initial 20° gloss	75	75

Examples 7 and 8

[0067] Poly(1,6-hexanediol β,β -styrenedicarboxylate) (Example 7) and poly(1,10-decanediol β,β -styrenedicarboxylate) (Example 8) were prepared by the process described in Example 4 but using equimolar amounts of 1,6-hexanediol (Example 7) or 1,10-decanediol (Example 8). Unplasticised coating films were prepared by the process of Example 4 using an equivalent amount of the polymer and the same amounts of PETMP and tributylamine and toluene as in Example 4. The properties of the films are shown in Table 3 below.

Table 3

	Example 7	Example 8
Tg of cured film by DSC	25°C	14°C
Tg of cured film by DMA	48°C	27°C
Linear swell (ethyl acetate)	10%	16%
Hydrolytic weight loss (1M NaOH, 1 week)	0	0
Initial 20° gloss	80	90

Example 9

[0068] Poly-(1,3-propanediol β,β -styrenedicarboxylate) was prepared by a modification of the procedure in "Organic Syntheses" (CFH Allen and FW Spangler Organic Synthesis, 1955, Coll. Vol. 3, 377-379), from poly-(1,3-propanediol malonate) and benzaldehyde, in the presence of benzoic acid (4 mol %) and piperidine (6 mol %), using toluene as solvent instead of benzene. Solvent was removed under reduced pressure (90°C/400 Pa), the product was dissolved in dichloromethane, and the solution was washed with water and aqueous sodium carbonate solution and dried (MgSO_4). Removal of solvent gave poly-(1,3-propanediol β,β -styrenedicarboxylate) as a clear gum (yield 92%), identified by NMR. Degree of polymerisation 4.6; molecular weight (Mn) 1140; olefin equivalent weight 252.

Curing of Poly-(1,3-propanediol β,β -styrenedicarboxylate) (PPDSDC) with Neopentylene Glycol Bis (acetoacetate) [NPGBAA]

[0069] PPDSDC (0.504g) was mixed with NPGBAA (0.271g) and then with 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.0185g) in the presence of ethyl acetate (0.126g) and 1-methoxy-5-propanol (0.074g). The polymer mixture (non-volatile content 80% w/w) was cast as a film and cured at ambient temperature (tack-free time 150 minutes). Crosslinked polymer properties are given in Table 4 [System PPDSDC/NPGBAA (DBU)].

[0070] By comparison, when trimethylolpropane triacrylate and a copolymer of β -methacryloxyethyl acetoacetate and butyl acrylate were cured using DBU under similar conditions. The tack-free time at ambient temperature was about 3 days.

Example 10

Poly-(1,3-propanediol 1-isopentene-1,1-dicarboxylate)

[0071] Poly-(1,3-propanediol 1-isopentene-1,1-dicarboxylate) was prepared by a modification of the procedure of Ravve et al. (J Polym Sci Polym Chem Ed, 1973, 11, 1733-1752), from poly-(1,3-propanediol malonate) and isobutyraldehyde, in the presence of isobutyric and benzoic acids (total acid 4 mole %) and piperidine (6 mole %), using 2.0 equivalents of aldehyde instead of 1.5 equivalents. Solvent (toluene) was removed under reduced pressure (50°C/

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2000 Pa), the product was dissolved in dichloromethane, and the solution was washed with aqueous sodium carbonate solution and water and dried (MgSO_4). Removal of solvent gave poly-(1,3-propanediol 1-isopentene-1,1-dicarboxylate) as a viscous liquid (yield 98%), identified by NMR. Degree of polymerisation 6.9; functionalisation of reactive sites 99%; olefinic functionality 7.6; molecular weight (Mn) 1520; olefin equivalent weight 203.

Curing of Poly-(1,3-propanediol 1-isopentene-1,1-dicarboxylate (PPDIDC) with Neopentylene Glycol Bis(acetoacetate) [NPGBAA]

[0072] PPDIDC was cured with NPGBAA in the presence of DBU and 1-methoxy-2-propanol using the procedure of Example 9. Cure behaviour was similar (tack-free time 150 minutes at ambient temperature) and the cured film had similar properties.

Example 11

Curing of Poly-(1,3-propanediol 1-isopentene-1,1-dicarboxylate) with Pentaerythritol Tetrakis-(β -mercaptopropionate) using Hindered Amine Light Stabiliser as Base Catalyst

[0073] Poly-(1,3-propanediol 1-isopentene-1,1-dicarboxylate) of Example 10 (2.00g) was mixed with pentaerythritol tetrakis-(β -mercaptopropionate) (1.20g, 2.46 mmol) and bis-(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate (Tinuvin 292 light stabiliser) (56 mg, 0.11 mmol) as amine catalyst, cast as a film and allowed to cure at ambient temperature. Gelation occurred after 20 minutes. The crosslinked polymer film had: Tg 43°C by DSC; sol content 2%; linear swell (ethyl acetate) 9%; hydrolytic weight loss (1M NaOH, 1 week) 1%; initial 60° gloss 98; gloss retention 95% after 1268 hours and 88% after 2034 hours UV exposure in a QUT test apparatus.

Example 12

[0074] Following the procedure of Example 10, poly-(1,6-hexanediol 1-isopentene-1,1-dicarboxylate) was prepared from poly-(1,6-hexanediol malonate) and isobutyraldehyde and was recovered as a viscous liquid (yield 94%), identified by NMR. Degree of polymerisation 5.9%; functionalisation of reactive sites 96%; olefinic functionality 6.1; molecular weight (Mn) 1510; olefin equivalent weight 247.

[0075] The polymer of Example 12 was cured with pentaerythritol tetrakis (β -mercaptopropionate) following the procedure and proportions of reagents and catalyst used in Example 11. It cured slightly more slowly than the polymer of Example 11 but had gelled within 30 minutes. The properties of the crosslinked polymer film were similar to those of the film of Example 11.

Example 13

[0076] Poly-(1,10-decanediol malonate) was prepared from dimethyl malonate (274.04g, 2.08 mol), 1,10-decanediol (323.64g, 1.86 mol) and titanium tetraisopropoxide (4.80g, 0.0169 mol) using the procedure of Example 4 and was recovered as a waxy solid (402.11g, yield 87%), identified by NMR. Degree of polymerisation 4.4; molecular weight (Mn) 1130; malonate equivalent weight 238.

[0077] Following the procedure of Example 9, poly-(1,10-decanediol β,β -styrenedicarboxylate) was prepared from poly-(1,10-decanediol malonate) and benzaldehyde and recovered as a viscous liquid (yield 95%), identified by NMR. Degree of polymerisation 4.3; functionalisation of reactive sites 94%; olefinic functionality 4.4; molecular weight (Mn) 1500; olefin equivalent weight 347.

Curing of Poly-(1,10-decanediol β,β -styrenedicarboxylate) with 1,1,1-Trimethylolpropane Tris(acetoacetate)

[0078] Poly-(1,10-decanediol β,β -styrenedicarboxylate) (Eq Wt 347; 2.450g, 7.21×10^{-3} gram-equivalents) was mixed with 1,1,1-trimethylolpropane tris(acetoacetate) (0.807g, 2.09 mmol) and ethyl α -sodio acetoacetate (0.035g, 3.02 mol%). The polymer mixture was cast as a film and allowed to cure at ambient temperature. Gelation occurred 40 minutes after mixing, and the film was tack-free overnight. The crosslinked polymer film had: Tg 16°C by DSC, Tg 26°C by DMA, 60° gloss 96 units.

Example 14

[0079] Following the procedure of Example 10, poly-(1,10-decanediol 1-isopentene-1,1-dicarboxylate) was prepared from poly-(1,10-decanediol malonate) and isobutyraldehyde and recovered as a viscous liquid (yield 88%), identified

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by NMR. Degree of polymerisation 4.6; functionalisation of reactive sites 95%; olefinic functionality 4.8; molecular weight (Mn) 1450; olefin equivalent weight 303.

Curing of Poly-(1,10-decanediol 1-isopentene-1,1-dicarboxylate) with 1,1,1-Trimethylolpropane Tris(acetoacetate)

[0080] Poly-(1,10-decanediol 1-isopentene-1,1-dicarboxylate (Eq Wt 303; 2.502g, 8.25×10^{-3} gram-equivalents) was mixed with 1,1,1-trimethylolpropane tris(acetoacetate) (1.023g, 2.65 mmol, 7.95×10^{-3} g-eq) and ethyl α -sodio acetoacetate (0.010g, 0.07 mmol, 0.84 mol%). The polymer mixture was cast as a film and allowed to cure at ambient temperature. Gelation occurred 15 minutes after mixing, and the film was tack-free overnight. The crosslinked polymer film had: Tg 14°C by DSC, Tg 31°C by DMA.

Example 15

Ethylene Bis[(diethyl phosphono) acetate]

[0081] Ethylene bis[(diethyl phosphono)acetate] was prepared by a modification of the procedure described in US Patent 3943200 employing a shorter reaction time and lower final temperature. To ethylene bis(chloroacetate) (107.5g, 0.5 mol) under nitrogen at 150°C triethyl phosphite (166.0g, 1.0 mol) was slowly added over 60 minutes with stirring, and the reaction mixture was maintained at 150°C for a further 3 hours. Continuous evolution of ethyl chloride occurred throughout the reaction. Removal of volatiles under vacuum gave ethylene bis [(diethyl phosphono) acetate] as a straw-coloured liquid (197.5g, 95%), identified by NMR.

Ethylene Bis[(diethyl α -phosphono)cinnamate]

[0082] A stirred solution of ethylene bis[(diethyl phosphono)acetate] (10.0g, 23.9 mmol), benzaldehyde (7.6g, 71.7 mmol) and piperidine (0.41g, 4.8 mmol) in toluene (100ml) was refluxed under nitrogen for 1 hour until no more water was collected in a Dean and Stark trap. The cooled reaction mixture was filtered through a silica gel plug, and removal of volatiles gave ethylene bis[(diethyl α -phosphono)cinnamate] as a yellow viscous oil (13.6g, 96%), identified by NMR.

Curing of Poly-[(n-butyl acrylate)-co-(β -methacryloyloxyethyl acetoacetate)] with ethylene bis [(diethyl α -phosphono) cinnamate]

[0083] A copolymer of n-butyl acrylate and β -acetoacetate in molar ratio 7:3 (2.00g, 3.7×10^{-3} gram-equivalents) was mixed with ethylene bis[(diethyl α -phosphono)cinnamate] (1.10g, 3.7×10^{-3} gram equivalents) and 1,8-diazabicyclo-[5.4.0] undec-7-ene (23 mg, 0.151 mmol) and allowed to cure at ambient temperature. Gelation occurred after 30 minutes. The crosslinked polymer film had 60° gloss 62 units, Tg 0°C by DSC, Tg 24°C by DMA.

Example 16

Curing of Poly-[(3-mercapto-1-propyl)methylsiloxane] with Ethylene bis [(diethyl α -phosphono)cinnamate]

[0084] Poly-[(3-mercapto-1-propyl)methylsiloxane] (2.00g, 14.9×10^{-3} gram-equivalents) was mixed with ethylene bis [(diethyl α -phosphono)-cinnamate] (4.40g, 14.9×10^{-3} gram-equivalents) and bis-(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate (60mg, 0.236×10^{-3} gram-equivalents) and allowed to cure at ambient temperature. Gelation occurred after 3 minutes. The crosslinked polymer film had Tg -4°C by DSC.

Example 17

Curing of Poly -(1,3-propanediol 1-isopentene-1,1-dicarboxylate) and Ethylene Bis [(diethyl α -phosphono)cinnamate] with Pentaerythritol Tetrakis -(β -mercaptopropionate)

[0085] Poly-(1,3-propanediol 1-isopentene-1,1-dicarboxylate) (1.80g, 8.82×10^{-3} gram-equivalents) was mixed with ethylene bis[(diethyl α -phosphono) cinnamate] (0.29g, 0.98×10^{-3} gram-equivalents), pentaerythritol tetrakis-(β -mercaptopropionate) (1.20g, 9.80×10^{-3} gram equivalents) and bis-(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate (56mg, 0.22×10^{-3} gram equivalents) and allowed to cure at ambient temperature. Gelation occurred after 10 minutes. The crosslinked polymer film had 60° gloss 77 units, Tg 3°C by DSC, Tg 12°C by DMA.

Example 18Ethylene bis[(diethyl 2-phosphono)-2-isohexenoate]

5 **[0086]** A stirred solution of ethylene bis [(diethyl phosphono)acetate] (10.0g, 23.9 mmol), isobutyraldehyde (10.0g, 138.7 mmol) and piperidine (0.50g, 5.87 mmol) in toluene (100 ml) was refluxed under nitrogen for 1 hour, after which further isobutyraldehyde (10.0g, 138.7 mmol) and piperidine (0.50g, 5.87 mmol) were added, and the reaction mixture was refluxed for another 2 hours, until no more water was collected in a Dean and Stark trap. The cooled reaction mixture was filtered through a silica gel plug, and removal of volatiles gave ethylene bis[(diethyl 2-phosphono)-2-isohexenoate] as a pale yellow viscous oil (12.3g, 98%), identified by NMR.

Curing of Poly-(1,3-propanediol 1-isopentene-1,1-dicarboxylate) and Ethylene Bis[(diethyl 2-phosphono)-2-isohexenoate] with Pentaerythritol Tetrakis-(β -mercaptopropionate)

15 **[0087]** Poly-(1,3-propanediol 1-isopentene-1,1-dicarboxylate) (1.80g, 8.82×10^{-3} gram-equivalents) was mixed with ethylene bis [(diethyl 2-phosphono)-2-isohexenoate](0.26g, 0.98×10^{-3} gram-equivalents), pentaerythritol tetrakis-(β -mercaptopropionate) (1.20g, 9.80×10^{-3} gram-equivalents) and bis-(1,2,2,6,6-pentamethyl-4-piperidyl) sebacate (56mg, 0.22×10^{-3} gram-equivalents) and allowed to cure at ambient temperature. Gelation occurred after 20 minutes. The crosslinked polymer film had 60° gloss 82 units, Tg 21°C by DSC.

Example 19

25 **[0088]** To 5-amino-2,2,4-trimethylcyclopentylmethylamine (127.72g, 0.819 mol) in xylene (525 ml) at 122°C was added with stirring 2,2,6-trimethyl-1,3-dioxen-4-one (232.51g, 1.637 mol) in xylene (525 ml) over 10 minutes, during which the temperature decreased to 104°C. After heating to 113°C over 5 minutes, vigorous effervescence and distillation of acetone (through a Vigreux column) commenced. Pot temperature was increased to 127°C over 5 minutes and to 140°C over a further 30 minutes, with collection of acetone distillate. After cooling to 39°C, dichloromethane was added, and removal of solvent and drying (93°C/100 Pa) gave 1-acetoacetamido-2-acetoacetamidomethyl-3,3,5-trimethylcyclopentane (237.03g, 89%), (AAMTCP), which was crushed to a light yellow powder, mp 94-114°C (mixture of stereoisomers), and identified by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FT-IR and Raman spectra.

30 **[0089]** Poly-(1,3-propanediol β,β -styrenedicarboxylate) (PPDSDC) (0.756 g) was mixed with AAMTCP (0.4855g) and then with 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) (0.027g) in the presence of 1-methoxy-2-propanol (0.402g). The polymer mixture (non-volatile content 76% w/w) was cast as a film and allowed to cure at ambient temperature. Gelation occurred 4 minutes after complete mixing, and the film was tack-free after 120 minutes. Crosslinked polymer film properties are given in Table 4 [System PPDSDC/AAMTCP(DBU)].

Example 20

40 **[0090]** Poly-(1,3-propanediol 1-isopentene-1,1-dicarboxylate) (PPDIDC) (0.616g) was mixed with AAMTCP (0.486g) and then with DBU (0.026g) in the presence of 1-methoxy-2-propanol (0.311g). The polymer mixture (non-volatile content 78% w/w) was cast as a film and allowed to cure at ambient temperature. Gelation occurred 2 minutes after complete mixing and the film was tack-free after 50 minutes. Crosslinked polymer film properties are given in Table 4 [System PPDIDC/AAMTCP (DBU)].

45 **[0091]** Similar quantities of oligomer and crosslinker were mixed together and then with tri-n-butylamine (0.055g) in the presence of 1-methoxy-2-propanol (0.3375g). The polymer mixture (non-volatile content 77% w/w) was cast as a film and allowed to cure at ambient temperature. Gelation occurred 10 minutes after complete mixing, and the film was tack-free overnight. Crosslinked polymer film properties are given in Table 4 [System PPDIDC/AAMTCP (TBA)].

Example 211-Acetoacetamido-3-acetoacetamidomethyl-3,5,5-trimethylcyclohexane

50 **[0092]** To isophoronediamine (139.24g, 0.819 mol) in xylene (525 ml) at 120°C was added with stirring 2,2,6-trimethyl-1,3-dioxen-4-one (232.51g, 1.637 mol) in xylene (525 ml) over 10 minutes, during which the temperature decreased to 103°C. Vigorous effervescence and distillation of acetone (through a Vigreux column) immediately commenced. Pot temperature was increased to 120°C over 15 minutes, and to 139°C over a further 30 minutes, with collection of acetone distillate. After cooling to 58°C, supernatant solution was separated from deposited gum, which was dissolved in dichloromethane. Removal of solvent from combined solutions and drying (91°C/100 Pa) gave 1-acetoacetamido-3-aceto-

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cetamidomethyl-3,5,5-trimethylcyclohexane (270.21g, 98%), (AAMTCH), which was crushed to a light yellow powder, mp 144-147°C (mixture of E and Z isomers), and identified by ¹H-NMR, ¹³C-NMR, FT-IR and Raman spectra.

[0093] PPDSDC (0.757g) was mixed with AAMTCH (0.507g) and then with DBU (0.026g) in the presence of 1-methoxy-2-propanol (0.527g). The polymer mixture (non-volatile content 71% w/w) was cast as a film and allowed to cure at ambient temperature. Gelation occurred 5 minutes after complete mixing, and the film was tack-free after 15 minutes. Crosslinked polymer film properties are given in Table 4 [System PPDSDC/AAMTCH (DBU)].

[0094] Similar quantities of oligmer and crosslinker were mixed together, and then with tri-n-butylamine (0.057g) in the presence of 1-methoxy-2-propanol (0.556g). The polymer mixture (non-volatile content 70% w/w) was cast as a film and allowed to cure at ambient temperature. Gelation occurred 5 minutes after complete mixing, and the film was tack-free overnight (20 hours). Crosslinked polymer film properties are given in Table 4 [System PPDSDC/AAMTCH (TBA)].

[0095] By comparison, an acetoacetate such as neopentyl glycol bis(acetoacetate) will not cure a Michael acceptor at ambient temperature using tributylamine as catalyst.

Example 22

N,N'Bis(acetoacetyl)-2-methylpiperazine

[0096] To 2-methylpiperazine (81.90g, 0.819 mol) in xylene (525 ml) at 133°C was added with stirring 2,2,6-trimethyl-1,3-dioxen-4-one (232.48g, 1.637 mol) in xylene (525 ml) over 10 minutes, during which the temperature decreased to 100°C. After heating to 115°C over 5 minutes vigorous effervescence commenced, and after heating to 124°C over another 5 minutes distillation of acetone (through a Vigreux column) also commenced. Pot temperature was increased to 139°C over a further 30 minutes, with collection of acetone distillate. After cooling to 20°C overnight, supernatant liquid was separated from deposited syrup, which was dissolved in dichloromethane. Removal of solvent from combined solutions and drying (92°C/100 Pa) gave N,N'-bis(acetoacetyl)-2-methylpiperazine (BAAMPZ) as a viscous syrup (216.66g, 99%), identified by ¹H-NMR, ¹³C-NMR, FT-IR and Raman spectra.

[0097] PPDSDC (0.757g) was mixed with BAAMPZ (0.403g) and then with DBU (0.028g) in the presence of 1-methoxy-2-propanol (0.1945g). The polymer mixture (non-volatile content 86% w/w) was cast as a film and allowed to cure at ambient temperature. Gelation occurred 5 minutes after complete mixing, and the film was tack-free after 30 minutes. Crosslinked polymer film properties are given in Table 4 [System PPDSDC/BAAMPZ (DBU)].

Example 23

N,N'-Bis (acetoacetyl)-1,4-diazacycloheptane

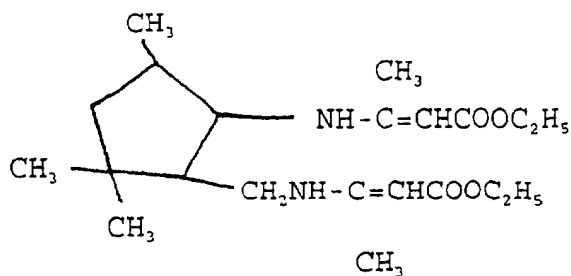
[0098] To 1,4-diazacycloheptane (81.90g, 0.819 mol) in xylene (525 ml) at 122°C was added with stirring 2,2,6-trimethyl-1,3-dioxen-4-one (232.49g, 1.637 mol) in xylene (525 ml) over 10 minutes, during which the temperature decreased to 99°C. After heating to 124°C over 5 minutes vigorous effervescence commenced, and after heating to 127°C over 5 minutes distillation of acetone (through a Vigreux column) also commenced. Pot temperature was increased to 140°C over a further 30 minutes, with collection of acetone distillate. After cooling to 15°C overnight, supernatant liquid was separated from deposited syrup, which was dissolved in dichloromethane. Removal of solvent from combined solutions and drying (91°C/100 Pa) gave N,N'-bis(acetoacetyl)-1,4-diazacycloheptane (BAADCH) as a viscous syrup (211.16g, 96%), identified by ¹H-NMR, ¹³C-NMR, FT-IR and Raman spectra.

[0099] BAADCH was cured with PPDSDC under the same conditions as described in Example 22. A tack-free film was formed after about an hour.

Example 24

1-(1-Ethoxycarbonyl-2-prop-1-enylamino)-2-(1-ethoxycarbonyl-2-prop-1-enylaminomethyl)-3,3,5-trimethylcyclopentane

[0100] To 5-amino-2,2,4-trimethylcyclopentylmethylamine (127.76g, 0.819 mol) in methanol (700 ml) was slowly added with stirring ethyl acetoacetate (215.85g, 1.660 mol) in methanol (700 ml) over 35 minutes, during which the temperature increased from 22°C to 31°C. The reaction mixture was allowed to stand at 21°C overnight (17 h). Further methanol was added, and removal of solvent and drying (91°/100 Pa) gave 1-(1-ethoxycarbonyl-2-prop-1-enylamino)-2-(1-ethoxycarbonyl-2-prop-1-enylaminomethyl) - 3,3,5-trimethylcyclopentane (EEMTCP, formula shown below) as a clear light yellow pourable viscous oil (296.54g, 95%) identified by ¹H-NMR, ¹³C-NMR, FT-IR and Raman spectra.



[0101] A mixture of EEMTCP and PPDIDC cured to a tack-free film within 48 hours even without catalyst.

Example 25

1-(1-isobutoxycarbonyl-2-prop-1-enylamino)-3-(1-isobutoxycarbonyl-2-prop-1-enylaminomethyl)-3,5,5-trimethylcyclohexane

[0102] To isophoronediamine (139.23g, 0.819 mol) in methanol (700 ml) was slowly added with stirring isobutyl acetoacetate (262.31g, 1.660 mol) in methanol (700 ml) over 45 minutes, during which the temperature increased from 22°C to 30°C. The reaction mixture was allowed to stand at 21°C overnight (15 h). Further methanol was added, and removal of solvent and drying (91°C/100 Pa) gave 1-(1-isobutoxycarbonyl-2-prop-1-enylamino)-3-(1-isobutoxycarbonyl-2-prop-1-enylaminomethyl)-3,5,5-trimethylcyclohexane (IIMTCH) as a clear light yellow viscous syrup (366.80g, 100%), which set to a soft gum on standing and was identified by ¹H-NMR, ¹³C-NMR, FT-IR and Raman spectra.

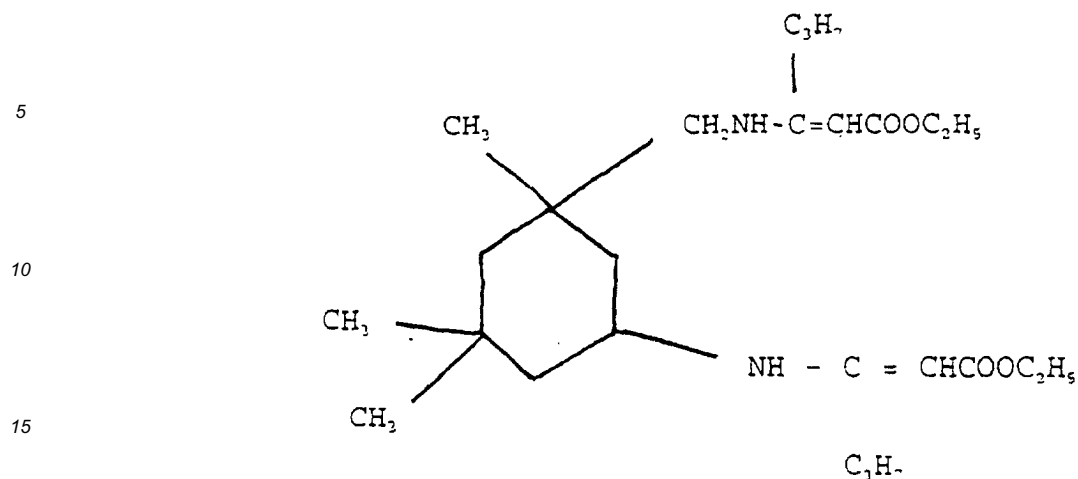
[0103] PPDIDC (0.6165g) was mixed with IIMTCH (0.6745g) in the presence of 1-methoxy-2-propanol (0.075g). The polymer mixture (non-volatile content 95% w/w) was cast as a film and allowed to cure at ambient temperature. Gelation occurred 30 minutes after complete mixing, and the film was tack-free after 24 hours. Crosslinked polymer film properties are given in Table 4 [System PPDIDC/IIMTCH].

[0104] Similar quantities of oligomer and crosslinker were mixed together, and then with triphenylphosphine (0.079g), in the presence of toluene (0.184g) and 1-methoxy-2-propanol (0.075g). The polymer mixture (non-volatile content 84% w/w) was cast as a film and allowed to cure at ambient temperature. Gelation occurred 45 minutes after complete mixing, and the film was tack-free after 24 hours. Crosslinked polymer film properties are given in Table 4 [System PPDIDC/IIMTCH (TPP)].

Example 26

1-(1-ethoxycarbonyl-2-pent-1-enylamino)-3-(1-ethoxycarbonyl-2-pent-1-enylaminomethyl)-3,5,5-trimethylcyclohexane

[0105] To isophoronediamine (139.23g, 0.819 mol) in methanol (700 ml) was slowly added with stirring ethyl butyrate (262.32g, 1.660 mol) in methanol (700 ml) over 45 minutes, during which the temperature decreased slightly from 24°C to 23°C. The reaction mixture was allowed to stand at 22°C overnight (16h). Further methanol was added, and removal of solvent and drying (91°C/100 Pa) gave 1-(1-ethoxycarbonyl-2-pent-1-enylamino)-3-(1-ethoxycarbonyl-2-pent-1-enylaminomethyl)-3,5,5-trimethylcyclohexane (EEMTCH formula shown below) as a clear light yellow pourable syrup (356.74g, 97%), identified by ¹H-NMR, ¹³C-NMR, FT-IR and Raman spectra.



20 **[0106]** PPDIDC and EEMTCH were cured without catalyst under the conditions described in Example. 25 and formed a tack-free film in 48 hours.

Example 27

25 Curing of Poly- (1,3-propanediol 1-isopentene-1,1-dicarboxylate) with 1,1,1-Trimethylolpropane Tris- β -(2-ethylhexylamino)crotonate generated in situ

30 **[0107]** 1,1,1-Trimethylolpropane tris (acetoacetate) (0.387g) was mixed with 2-ethylhexylamine (0.386g) and then with PPDIDC (0.616g). The polymer mixture (non-volatile content 100% w/w) was cast as a film and allowed to cure at ambient temperature. Gelation occurred overnight (15 hours), and the film was tack-free after 72 hours. Crosslinked polymer film properties are given in Table 4 [System PPDIDC/TMPTAA/EHA].

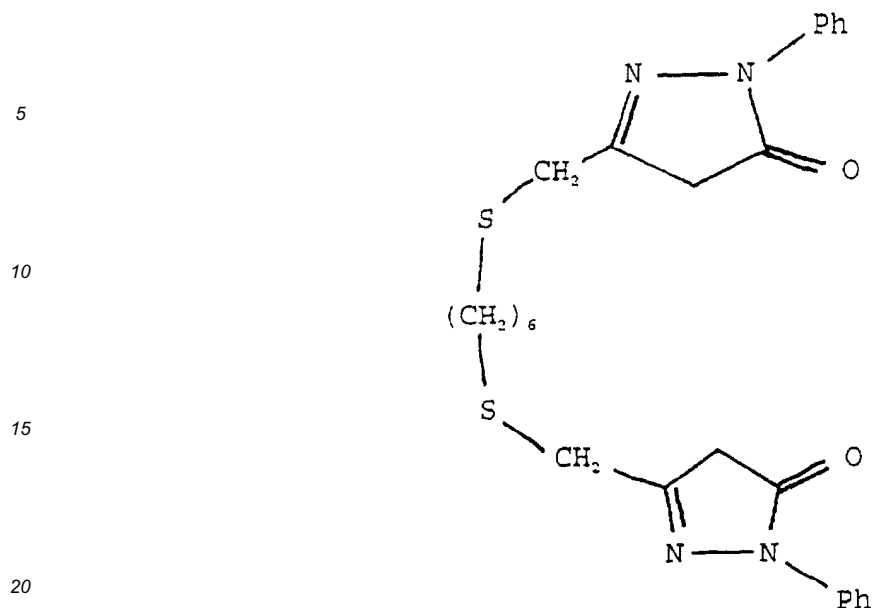
Example 28

35 Dimethyl 3,14-Dioxo-5,12-dithia-1,16-hexadecanedioate

40 **[0108]** To methyl gamma-chloroacetoacetate (199.72g, 1.327 mol) in isopropanol (350 ml) at 20°C was added with stirring 1,6-hexanedithiol (98.75g, 0.658 mol) in isopropanol (350 ml) over 5 minutes, followed by isopropanol washings (270 ml) over a further 5 minutes. To the resulting solution at 22°C was added dropwise sodium hydroxide (52.55g, 1.314 mol) in methanol (650 ml) over 60 minutes, during which the temperature increased to 31°C, followed by addition at 30°C of methanol washings (80 ml) over 5 minutes. The milky suspension was stirred at 27°C for another 60 minutes, and then allowed to stand at 21°C overnight (16 hours). The suspension was again stirred at 21°C for 3 hours, during which complete reaction was confirmed by thin-layer chromatography. Water was added to give a two-phase liquid mixture, which was extracted with dichloromethane, and the combined organic phases were dried (Na₂SO₄). Removal of solvent and drying (86°C/100 Pa) gave dimethyl 3,14-dioxo-5,12-dithia-1,16-hexadecanedioate CH₃OOCCH₂COCH₂S(CH₂)₆SCH₂COCH₂COOCH₃ as a mobile oil (248.55g, yield 100%, purity 99% by NMR).

1,10-Bis-(1-phenyl-5-oxo-3-pyrazolinyl)-2,9-dithiadecane

50 **[0109]** To dimethyl 3,14-dioxo-5,12-dithia-1,16-hexadecanedioate (209.58g, 0.554 mol) in methanol (850 ml) at 20°C was added with stirring phenylhydrazine (124.00g, 1.148mol) in isopropanol (510 ml) over 15 minutes, during which the temperature increased to 39°C. The reaction mixture was heated to 60°C over 25 minutes and maintained at 63°C for a further 90 minutes. After cooling to 20°C overnight (17.5 hours), much solid had crystallised from solution. The reaction mixture was stirred at 21°C for 4.5 hours, and the thick suspension was then filtered to separate solid. The solid was washed with methanol/isopropanol (280:170 v/v, 2 x 450 ml) until washings were virtually colourless, sucked dry on a filter, and then dried under vacuum to constant weight, to give 1,10-bis-(1-phenyl-5-oxo-3-pyrazolinyl)-2,9-dithiadecane (BPOPDD) (formula shown below) (199.26g, 73%) as a pale brown powder, mp 136-137°C, identified by ¹H-NMR, ¹³C-NMR, FT-IR and Raman spectra.



25 **[0110]** PPDSDC (0.504g) was mixed with BPOPDD (0.494g) and then with tri-n-butylamine (0.037g) in the presence of cyclohexanone (0.741g) and 1-methoxy-2-propanol (0.213g). The polymer mixture (non-volatile content 52% w/w) was cast as a film and cured at either 17°C (gel time 25 minutes) or 89°C (tack-free time 15 minutes). Crosslinked polymer film properties are given in Table 4 [System PPDSDC/BPOPDD (TBA)].

30 **[0111]** Similar quantities of oligomer and crosslinker were mixed together, and then with DBU (0.019g) in the presence of cyclohexanone (0.741g) and 1-methoxy-2-propanol (0.202g). The polymer mixture (non-volatile content 52% w/w) was cast as a film and cured at either 17°C (gel time 30 minutes) or 89°C (tack-free time 15 minutes). Crosslinked polymer film properties are given in Table 4. [System PPDSDC/BPOPDD (DBU)].

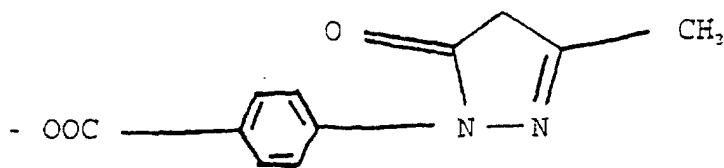
Example 29

35 **[0112]** PPDSDC (0.757g) was mixed with a solution of BPOPDD (0.106g) in Trimethylolpropane Tris(acetoacetate) (TMPTAA, 0.331g), and then with DBU (0.028g) in the presence of 1-methoxy-2-propanol (0.196g). The polymer mixture (non-volatile content 86% w/w) was cast as a film and cured at ambient temperature (gel time 20 minutes). Crosslinked polymer film properties are given in Table 4 [System PPDSDC/BPOPDD/TMPTAA (DBU)].

Example 30

40 Poly-[(hydrogenated linoleic dimer acid)-co-(3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate)] (2:3) bis-[p-(3-methyl-5-oxo-1-pyrazolinyl) benzoate]

45 **[0113]** To a stirred mobile slurry of p-(3-methyl-5-oxo-1-pyrazolinyl)-benzoic acid(24.2g, 0.111 mol) in hydrogenated linoleic dimer acid (62.59g, 0.111 mol) and 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate (41.96g, 0.167 mol) at 22°C under nitrogen was added benzyltrimethylammonium hydroxide in methanol (40% w/w, 4.171g, 9.99 mmol, 3.00 mol%), followed after 5 minutes by addition at 23°C of xylene washings (7.5 ml). The reaction mixture was heated to 125°C over 15 minutes and maintained at 122°C for 5 hours, changing from suspension to opaque viscous liquid. After cooling to 37°C, dichloromethane was added, the viscous solution was washed with water, the aqueous phase was washed with dichloromethane, and the combined dichloromethane phases were dried (Na₂SO₄).
50 Removal of solvent and drying (91°C/100 Pa) gave poly-[(hydrogenated linoleic dimer acid)-co-(3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate)] (2:3) bis-[p-(3-methyl-5-oxo-1-pyrazolinyl)benzoate] (PDEBPB) as a clear hard glassy gum (111.99g, 87%), identified by ¹H-NMR, ¹³C-NMR, FT-IR and Raman spectra. This was a polyester having terminal
55



groups.

10 **[0114]** PPDSDC (0.2520 was mixed with PDEBPB (1.160g) and then with tri-n-butylamine (0.019g) in the presence of ethylacetate (0.497g) and 1-methoxy-2-propanol (0.073g). The polymer mixture (non-volatile content 72% w/w) was cast as a film, and cured at ambient temperature (gel time 2 minutes). Crosslinked polymer film properties are given in Table 4 [System PPDSDC/PDEBPB (TBA)]

15 **[0115]** Similar quantities of PPDSDC and PDEBPB were mixed together, and then with DBU (0.0095g) in the presence of ethyl acetate (0.497g) and 1-methoxy-2-propanol (0.066g). The polymer mixture (non-volatile content 72% w/w) was cast as a film and cured at ambient temperature (gel time 2 minutes). Crosslinked polymer film properties are given in Table 4 [System PPDSDC/PDEBPB (DBU)].

Example 31

20 **[0116]** PPDIDC (0.206g) was mixed with PDEBPB (1.160g) and then with tri-n-butylamine (0.019g) in the presence of ethyl acetate (0.497g) and 1-methoxy-2-propanol (0.044g). The polymer mixture (non-volatile content 72% w/w) was cast as a film and cured at ambient temperature (gel time 2 minutes). Crosslinked polymer film properties are given in Table 4 [System PPDIDC/PDEBPB(TBA)].

25 **[0117]** Similar quantities of PPDIDC and PDEBPB were mixed together, and then with DBU (0.010g) in the presence of ethyl acetate (0.497g) and 1-methoxy-2-propanol (0.039g). The polymer mixture (non-volatile content 72% w/w) was cast as a film and cured at ambient temperature (gel time 2 minutes). Crosslinked polymer film properties are given in Table 4 [System PPDIDC/PDEBPB(DBU)].

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Film Properties of Cured Polyester Olefin/Carbon Nucleophile Systems

Example No.	System	Gloss Units (aluminium substrate)		Gloss Units (PTFE substrate)		DSC	DMA	Tg °C
		20°	60°	20°	60°			
9	PPDSDC/NPGBAA (DBU)	38	98	-	-	10	-	-
19	PPDSDC/AAMTCP (DBU)	23	65	82	96	3	32	-
20	PPDIDC/AAMTCP (DBU)	31	85	76	91	-2	33	-
20	PPDIDC/AAMTCP (TBA)	21	54	39	69	-29	-	-
21	PPDSDC/AAMTCH (DBU)	47	105	64	94	28	58	-
21	PPDSDC/AAMTCH (TBA)	26	74	83	94	-3	-	-
22	PPDSDC/BAAMPZ (DBU)	27	60	87	96	18	57	-
25	PPDIDC/IIMTCH	85	137	81	87	32	-	-
25	PPDIDC/IIMTCH (TPP)	75	122	60	89	28	39	-
27	PPDIDC/TMPTAA/EHA	61	112	62	83	-13	15	-
28	PPDSDC/BPOPDD (DBU)	35	92	-	-	-3	-	-
28	PPDSDC/BPOPDD (TBA)	81	114	-	-	-7	-	-
29	PPDSDC/BPOPDD/TMPTAA (DBU)	19	63	-	-	-	-	-
30	PPDSDC/PDEBFB (DBU)	27	68	-	-	5	-	-
30	PPDSDC/PDEBFB (TBA)	23	55	-	-	10	-	-
31	PPDIDC/PDEBFB (DBU)	21	63	-	-	10	-	-
31	PPDIDC/PDEBFB (TBA)	14	54	-	-	10	-	-

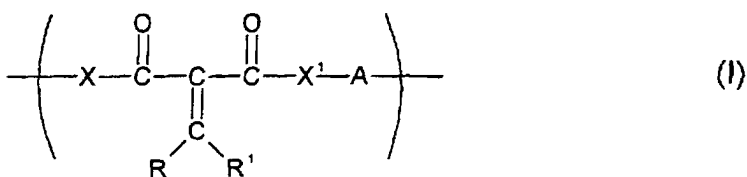
Claims

1. A coating, adhesive or sealant composition curable by Michael reaction comprising (A) a Michael acceptor which

EP 0 970 137 B9 (W1B1)

is a compound or polymer containing at least two activated olefinic double bonds and (B) a Michael donor which is a compound or polymer containing at least two nucleophilic groups, **characterised in that** the Michael acceptor (A) is a polymer having repeating units of the formula:

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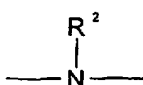
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where R is hydrogen or an alkyl or aryl group which is optionally substituted and R¹ is hydrogen or an alkyl group which is optionally substituted;

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X and X¹ are each selected from an oxygen atom or a group of the formula

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where R² is hydrogen or an alkyl or aryl group which is optionally substituted; and A is a divalent organic group.

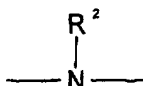
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2. A coating, adhesive or sealant composition according to claim 1 **characterised in that** the Michael acceptor (A) is a polyester in which the groups X and X¹ represent oxygen atoms.

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3. A coating, adhesive or sealant composition according to claim 1 **characterised in that** the Michael acceptor (A) is a polyamide in which the groups X and X¹ represent groups of the formula

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where R² is hydrogen or an alkyl group.

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4. A coating, adhesive or sealant composition curable by Michael reaction comprising (A) a Michael acceptor which is a compound or polymer containing at least two activated olefinic double bonds and (B) a Michael donor which is a compound or polymer containing at least two nucleophilic groups, **characterised in that** the Michael acceptor (A) is a polymer containing at least two groups of the formula:

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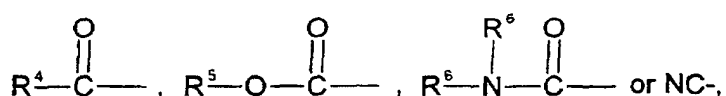
where A¹ is a divalent organic group or a linking bond whereby the group (II) is linked to the compound or polymer (A);

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R³ is hydrogen or an alkyl group; and

E and E¹ are each electron-withdrawing groups selected from groups of the formula:

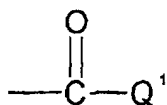
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where R⁴ and R⁵ each represent an optionally substituted alkyl or aryl group and each group R⁶ represents a

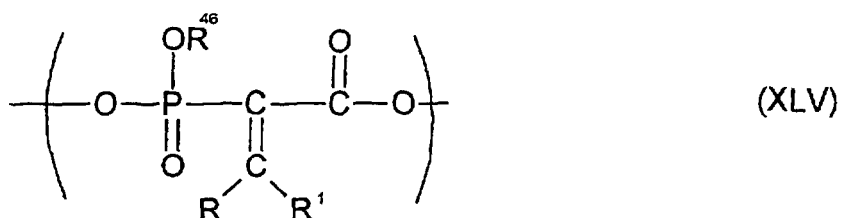
hydrogen atom or an optionally substituted alkyl or aryl group.

5. A coating, adhesive or sealant composition according to claim 4, **characterised in that** the groups E and E¹ are each acyl groups of the formula



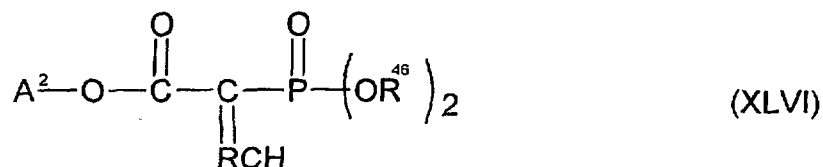
where Q¹ is an optionally substituted alkyl or aryl group.

6. A coating, adhesive or sealant composition curable by Michael reaction and comprising (A) a Michael acceptor which is a compound or polymer containing at least two activated olefinic double bonds and (B) a Michael donor which is a compound or polymer containing at least two nucleophilic groups, **characterised in that** the Michael acceptor (A) is a compound or polymer containing at least two groups of the formula:



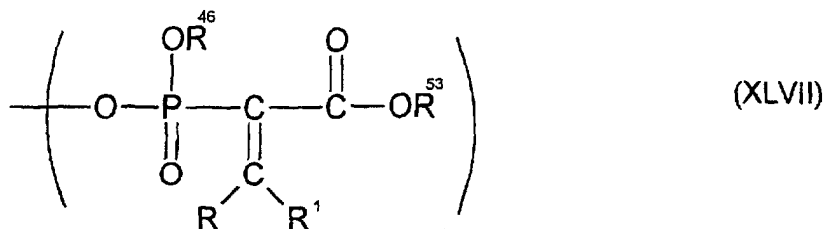
where R and R¹ are defined as in claim 1 and R⁴⁶ is an alkyl or aryl group which is optionally substituted.

7. A coating, adhesive or sealant composition according to claim 6, **characterized in that** the Michael acceptor contains at least two groups of the formula



where A² is the residue of a polyol A²(OH)_n.

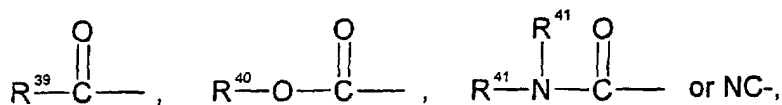
8. A coating, adhesive or sealant composition according to claim 6, **characterized in that** the Michael acceptor contains at least two groups of the formula



where R⁵³ is an alkyl or aryl group which is optionally substituted.

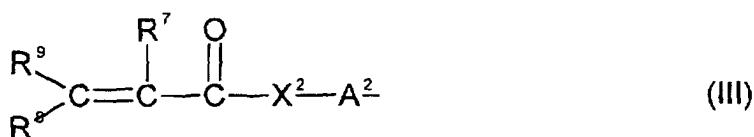
9. A coating, adhesive or sealant composition according to any of claims 1 to 8, **characterized in that** the nucleophilic

groups of the Michael donor are selected from thiol groups, primary or secondary amine groups and active hydrogen groups of the formula Y-CH-Y¹, where Y and Y¹ are each selected from groups of the formula:

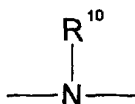


where R³⁹ and R⁴⁰ each represent an alkyl or aryl group and each group R⁴¹ is a hydrogen atom or an alkyl group.

10. A coating, adhesive or sealant composition curable by Michael reaction and comprising (A) a Michael acceptor which is a compound or polymer containing at least two activated olefinic double bonds and (B) a Michael donor which is a compound or polymer containing at least two nucleophilic groups, **characterised in that** the Michael acceptor (A) is a compound or polymer containing at least two doubly activated olefinic groups of the formula:

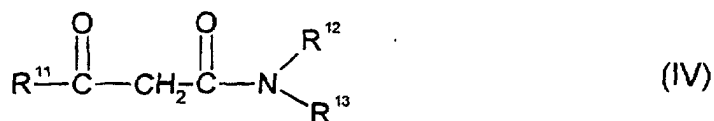


where R⁷ is an electron-withdrawing group, R⁸ and R⁹ are each independently selected from hydrogen, alkyl, which is optionally substituted, and aryl, which is optionally substituted, X² is an -O- or



group, where R¹⁰ is hydrogen or an alkyl group; and A² is an optionally substituted alkylene group linking the doubly activated olefinic group to the compound or polymer (A); and **in that** the nucleophilic group of the Michael donor (B) are

- (i) beta-ketoamide groups of the formula

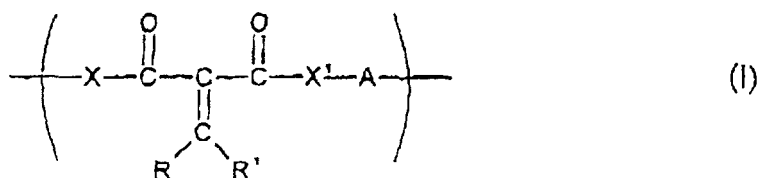


where at least one of the groups R¹¹, R¹², and R¹³ is an optionally substituted alkylene or arylene radical whereby the ketoamide group is linked to the compound or polymer (B) and the remaining groups R¹¹, R¹², and R¹³ are in the case of R¹¹ an optionally substituted alkyl or aryl group and in the case of R¹² and R¹³ a hydrogen atom or an optionally substituted alkyl or aryl group, provided that at least one of R¹² and R¹³ is other than aryl or arylene, or

- (ii) enamine beta-carboxylate groups of the formula

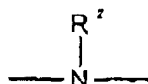
Patentansprüche

1. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung, die durch eine Michael-Reaktion härtbar ist und folgendes umfasst: (A) einen Michael-Acceptor, bei dem es sich um eine Verbindung oder ein Polymer mit wenigstens zwei aktivierten olefinischen Doppelbindungen handelt; und (B) einen Michael-Donor, bei dem es sich um eine Verbindung oder ein Polymer mit wenigstens zwei nucleophilen Gruppen handelt, **dadurch gekennzeichnet, dass** der Michael-Acceptor (A) ein Polymer ist, das Repetiereinheiten der Formel



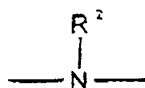
aufweist, wobei R Wasserstoff oder eine gegebenenfalls substituierte Alkyl- oder Arylgruppe ist und R¹ Wasserstoff oder eine gegebenenfalls substituierte Alkylgruppe ist;

X und X¹ jeweils aus einem Sauerstoffatom oder einer Gruppe der Formel



ausgewählt sind, wobei R² Wasserstoff oder eine gegebenenfalls substituierte Alkyl- oder Arylgruppe ist; und A eine zweiwertige organische Gruppe ist.

2. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung gemäß Anspruch 1, **dadurch gekennzeichnet, dass** der Michael-Acceptor (A) ein Polyester ist, bei dem die Gruppen X und X¹ Sauerstoffatome darstellen.
3. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung gemäß Anspruch 1, **dadurch gekennzeichnet, dass** der Michael-Acceptor (A) ein Polyamid ist, bei dem die Gruppen X und X¹ Gruppen der Formel



darstellen, wobei R² Wasserstoff oder eine Alkylgruppe ist.

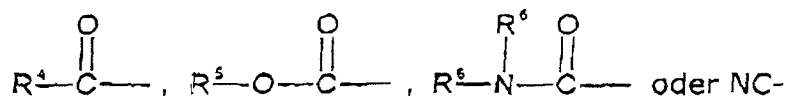
4. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung, die durch eine Michael-Reaktion härtbar ist und folgendes umfasst: (A) einen Michael-Acceptor, bei dem es sich um eine Verbindung oder ein Polymer mit wenigstens zwei aktivierten olefinischen Doppelbindungen handelt; und (B) einen Michael-Donor, bei dem es sich um eine Verbindung oder ein Polymer mit wenigstens zwei nucleophilen Gruppen handelt, **dadurch gekennzeichnet, dass** der Michael-Acceptor (A) ein Polymer ist, das wenigstens zwei Gruppen der Formel



enthält, wobei A¹ eine zweiwertige organische Gruppe oder eine verknüpfende Bindung, mit der die Gruppe (II)

mit der Verbindung bzw. dem Polymer (A) verknüpft ist, ist;
 R^3 Wasserstoff oder eine Alkylgruppe ist; und
 E und E^1 jeweils elektronenziehende Gruppen sind, die aus Gruppen der Formel

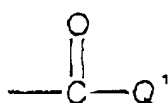
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10 ausgewählt sind, wobei R^4 und R^5 jeweils eine gegebenenfalls substituierte Alkyl- oder Arylgruppe darstellen und jede Gruppe R^6 ein Wasserstoffatom oder eine gegebenenfalls substituierte Alkyl- oder Arylgruppe darstellt.

- 15 5. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung gemäß Anspruch 4, **dadurch gekennzeichnet, dass** die Gruppen E und E^1 jeweils Acylgruppen der Formel

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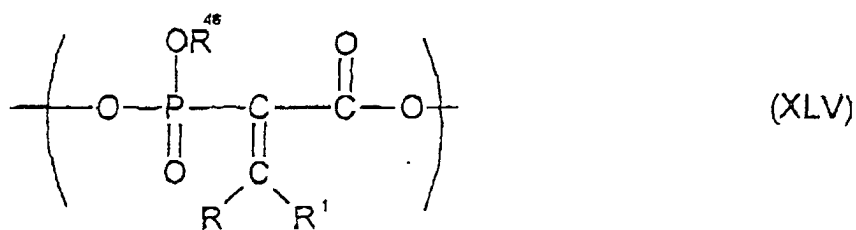


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sind, wobei Q^1 eine gegebenenfalls substituierte Alkyl- oder Arylgruppe ist.

- 25 6. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung, die durch eine Michael-Reaktion härtbar ist und folgendes umfasst: (A) einen Michael-Acceptor, bei dem es sich um eine Verbindung oder ein Polymer mit wenigstens zwei aktivierten olefinischen Doppelbindungen handelt; und (B) einen Michael-Donor, bei dem es sich um eine Verbindung oder ein Polymer mit wenigstens zwei nucleophilen Gruppen handelt, **dadurch gekennzeichnet, dass** der Michael-Acceptor (A) eine Verbindung oder ein Polymer ist, die bzw. das wenigstens zwei Gruppen der Formel

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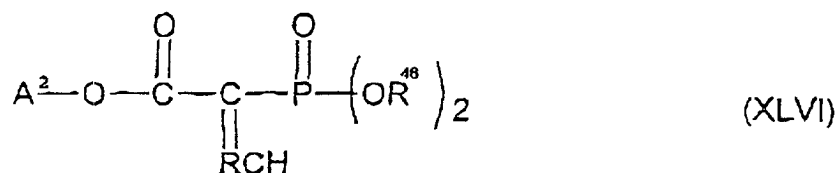
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enthält, wobei R und R^1 wie in Anspruch 1 definiert sind und R^{46} eine gegebenenfalls substituierte Alkyl- oder Arylgruppe ist.

- 45 7. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung gemäß Anspruch 6, **dadurch gekennzeichnet, dass** der Michael-Acceptor wenigstens zwei Gruppen der Formel

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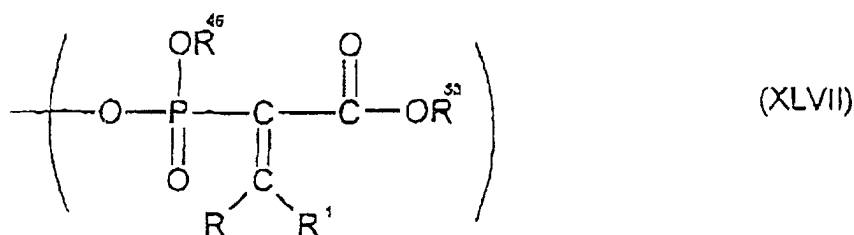


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enthält, wobei A^2 der Rest eines Polyols $A^2(\text{OH})_n$ ist.

8. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung gemäß Anspruch 6, **dadurch gekennzeichnet,**

dass der Michael-Acceptor wenigstens zwei Gruppen der Formel



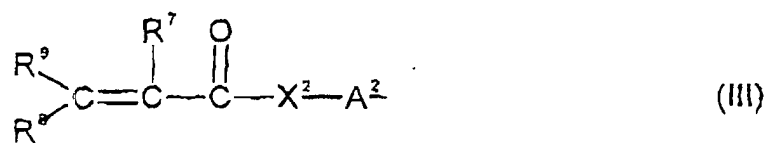
enthält, wobei R^{53} eine gegebenenfalls substituierte Alkyl- oder Arylgruppe ist.

9. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung gemäß einem der Ansprüche 1 bis 8, **dadurch gekennzeichnet, dass** die nucleophilen Gruppen des Michael-Donors aus Thiolgruppen, primären oder sekundären Amingruppen und aktiven Wasserstoff enthaltenden Gruppen der Formel $\text{Y}-\text{CH}-\text{Y}^1$ ausgewählt sind, wobei Y und Y^1 jeweils aus Gruppen der Formel

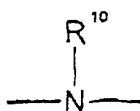


ausgewählt sind, wobei R^{39} und R^{40} jeweils eine Alkyl- oder Arylgruppe darstellen und jede Gruppe R^{41} ein Wasserstoffatom oder eine Alkylgruppe ist.

10. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung, die durch eine Michael-Reaktion härtbar ist und folgendes umfasst; (A) einen Michael-Acceptor, bei dem es sich um eine Verbindung oder ein Polymer mit wenigstens zwei aktivierten olefinischen Doppelbindungen handelt; und (B) einen Michael-Donor, bei dem es sich um eine Verbindung oder ein Polymer mit wenigstens zwei nucleophilen Gruppen handelt, **dadurch gekennzeichnet, dass** der Michael-Acceptor (A) eine Verbindung oder ein Polymer ist, die bzw. das wenigstens zwei doppelt aktivierte olefinische Gruppen der Formel



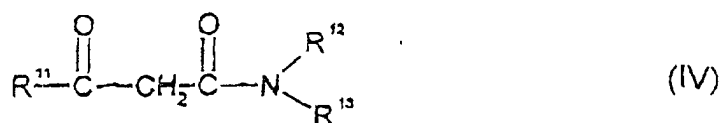
enthält, wobei R^7 eine elektronenziehende Gruppe ist, R^8 und R^9 jeweils unabhängig aus Wasserstoff, gegebenenfalls substituiertem Alkyl und gegebenenfalls substituiertem Aryl ausgewählt sind, X^2 eine Gruppe -O- oder



ist, wobei R^{10} Wasserstoff oder eine Alkylgruppe ist; und A^2 eine gegebenenfalls substituierte Alkylengruppe ist, die die doppelt aktivierte olefinische Gruppe mit der Verbindung bzw. dem Polymer (A) verknüpft; und dadurch,

dass es sich bei der nucleophilen Gruppe des Michael-Donors (B) um

(i) beta-Ketoamidgruppen der Formel



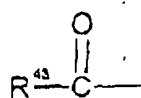
handelt, wobei wenigstens eine der Gruppen R^{11} , R^{12} und R^{13} ein gegebenenfalls substituierter Alkyl- oder Arylenrest ist, über den die Ketoamidgruppe mit der Verbindung bzw. dem Polymer (B) verknüpft ist, und die übrigen Gruppen R^{11} , R^{12} und R^{13} im Falle von R^{11} eine gegebenenfalls substituierte Alkyl- oder Arylgruppe ist und im Falle von R^{12} und R^{13} ein Wasserstoffatom oder eine gegebenenfalls substituierte Alkyl- oder Arylgruppe sind, mit der Maßgabe, dass wenigstens einer der Reste R^{12} und R^{13} kein Aryl oder Arylen ist; oder

(ii) Enamin-beta-carboxylat-Gruppen der Formel

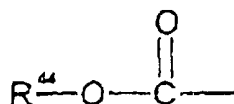


wobei wenigstens eine der Gruppen R^{18} , R^{19} und R^{20} ein gegebenenfalls substituierter Alkylrest ist oder R^{18} ein gegebenenfalls substituierter Arylenrest ist, über den die Enamin-carboxylat-Gruppe mit der Verbindung bzw. dem Polymer (B) verknüpft ist, und von den übrigen Gruppen R^{18} ein Wasserstoffatom oder eine gegebenenfalls substituierte Alkyl- oder Arylgruppe ist, R^{19} ein Wasserstoffatom oder eine gegebenenfalls substituierte Alkylgruppe ist und R^{20} eine gegebenenfalls substituierte Alkylgruppe ist.

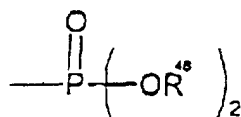
11. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung gemäß Anspruch 10, **dadurch gekennzeichnet, dass** die elektronenziehenden Gruppen des Michael-Acceptors (A) aus -CN, Acylgruppen der Formel



wobei R^{43} eine gegebenenfalls substituierte Alkyl- oder Arylgruppe ist, Estergruppen der Formel



wobei R^{44} eine gegebenenfalls substituierte Alkyl- oder Arylgruppe ist, Amidgruppen der Formel $-\text{CON}(\text{R}^{45})_2$, wobei jede Gruppe R^{45} , die gleich oder verschieden sein können, aus Wasserstoff und gegebenenfalls substituiertem Alkyl oder Aryl ausgewählt ist, und Phosphorsäureestergruppen der Formel

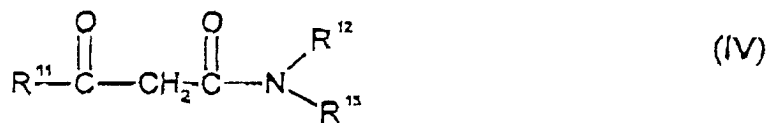


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10 wobei R⁴⁶ eine gegebenenfalls substituierte Alkyl- oder Arylgruppe ist, ausgewählt sind.

12. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung gemäß Anspruch 9 oder 10, **dadurch gekennzeichnet, dass** die nucleophilen Gruppen des Elektronendonors (B) beta-Ketoamidgruppen der Formel

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sind, wie sie in Anspruch 10 definiert sind.

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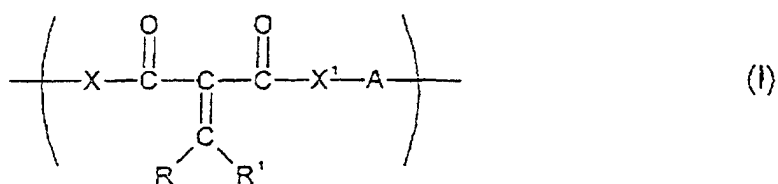
13. Beschichtungs-, Klebstoff- oder Dichtungszusammensetzung gemäß einem der Ansprüche 1 bis 12, die einen Katalysator in Form eines tertiärenamins enthält, **dadurch gekennzeichnet, dass** der Katalysator ein sterisch gehindertertes tertiäres Amin ist, das als Lichtstabilisator wirken kann.

Revendications

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1. Composition de revêtement, d'adhésif ou de produit d'étanchéité vulcanisable par la réaction de Michael comprenant (A) un accepteur de Michael qui est un composé ou un polymère contenant au moins deux doubles liaisons oléfiniques activées et (B) un donneur de Michael qui est un composé ou un polymère contenant au moins deux groupes nucléophiles, **caractérisée en ce que** l'accepteur de Michael (A) est un polymère possédant des unités répétées de formule :

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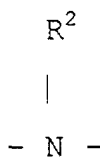
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où R est l'hydrogène ou un groupe alkyle ou aryle qui est éventuellement substitué et R¹ est l'hydrogène ou un groupe alkyle qui est éventuellement substitué ;

X et X¹ sont chacun sélectionné à partir d'un atome d'oxygène ou un groupe de formule :

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où R² est l'hydrogène ou un groupe alkyle ou aryle qui est éventuellement substitué ; et
A est un groupe organique divalent.

2. Composition de revêtement, d'adhésif ou de produit d'étanchéité selon la revendication 1, **caractérisée en ce que** l'accepteur de Michael (A) est un polyester dans lequel les groupes X et X¹ représentent des atomes d'oxygène.

3. Composition de revêtement, d'adhésif ou de produit d'étanchéité selon la revendication 1, **caractérisée en ce que** l'accepteur de Michael (A) est un polyamide dans lequel les groupes X et X¹ représentent des groupes de formule

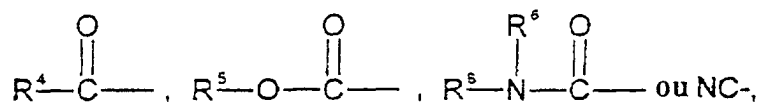


où R² est l'hydrogène ou un groupe alkyle.

4. Composition de revêtement, d'adhésif ou de produit d'étanchéité vulcanisable par la réaction de Michael comprenant (A) un accepteur de Michael qui est un composé ou un polymère contenant au moins deux doubles liaisons oléfiniques activées et (B) un donneur de Michael qui est un composé ou un polymère contenant au moins deux groupes nucléophiles, **caractérisée en ce que** l'accepteur de Michael (A) est un polymère contenant au moins deux groupes de formule :

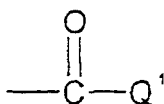


où A¹ est un groupe organique divalent ou une liaison par laquelle le groupe (II) est lié au composé ou polymère (A) ;
R³ est l'hydrogène ou un groupe alkyle ; et
E et E¹ sont chacun des groupes capteurs d'électrons sélectionnés parmi les groupes de formule :



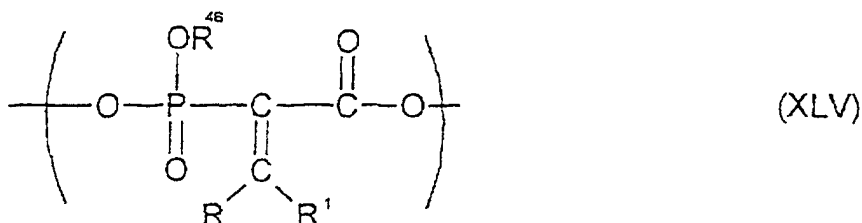
où R⁴ et R⁵ représentent chacun un groupe alkyle ou aryle éventuellement substitué et chaque groupe R⁶ représente un atome d'hydrogène ou un groupe alkyle ou aryle éventuellement substitué.

5. Composition de revêtement, d'adhésif ou de produit d'étanchéité selon la revendication 4, **caractérisée en ce que** les groupes E et E¹ sont chacun des groupes acyle de formule



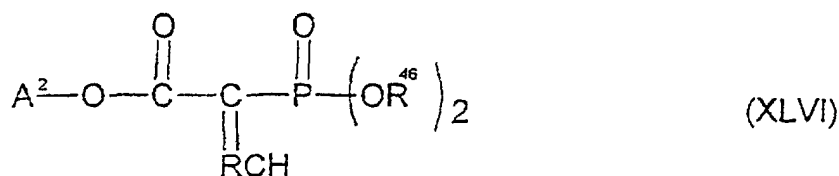
où Q¹ est un groupe alkyle ou aryle éventuellement substitué.

6. Composition de revêtement, d'adhésif ou de produit d'étanchéité vulcanisable par la réaction de Michael comprenant (A) un accepteur de Michael qui est un composé ou un polymère contenant au moins deux doubles liaisons oléfiniques activées et (B) un donneur de Michael qui est un composé ou un polymère contenant au moins deux groupes nucléophiles, **caractérisée en ce que** l'accepteur de Michael (A) est un composé ou un polymère contenant au moins deux groupes de formule :



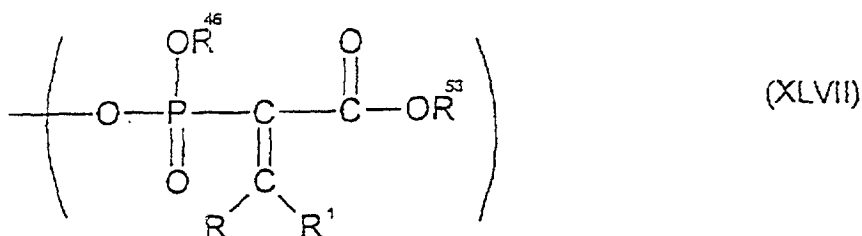
où R et R¹ sont définis selon la revendication 1 et R⁴⁶ est un groupe alkyle ou aryle éventuellement substitué.

7. Composition de revêtement, d'adhésif ou de produit d'étanchéité selon la revendication 6, **caractérisée en ce que** l'accepteur de Michael contient au moins deux groupes de formule



où A² est le résidu d'un polyol A²(OH)_n.

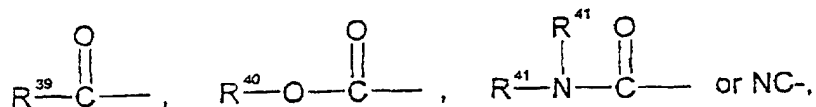
8. Composition de revêtement, d'adhésif ou de produit d'étanchéité selon la revendication 6, **caractérisée en ce que** l'accepteur de Michael contient au moins deux groupes de formule



où R⁵³ est un groupe alkyle ou aryle éventuellement substitué.

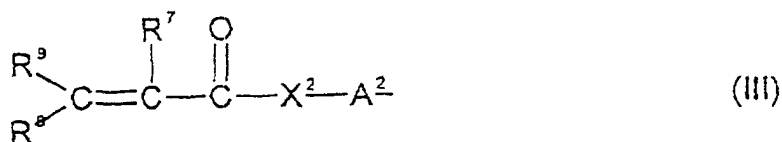
9. Composition de revêtement, d'adhésif ou de produit d'étanchéité selon l'une quelconque des revendications 1 à 8, **caractérisée en ce que** les groupes nucléophiles du donneur de Michael sont sélectionnés à partir de groupes

thiol, de groupes amine primaire ou secondaire et de groupes d'hydrogène actif de formule Y-CH-Y¹, où Y et Y¹ sont chacun sélectionnés à partir de groupes de formule :

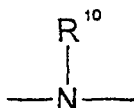


où R³⁹ et R⁴⁰ représentent chacun un groupe alkyle ou aryle et chaque groupe R⁴¹ est un atome d'hydrogène ou un groupe alkyle.

10. Composition de revêtement, d'adhésif ou de produit d'étanchéité vulcanisable par la réaction de Michael comprenant (A) un accepteur de Michael qui est un composé ou un polymère contenant au moins deux doubles liaisons oléfiniques activées et (B) un donneur de Michael qui est un composé ou un polymère contenant au moins deux groupes nucléophiles, **caractérisée en ce que** l'accepteur de Michael (A) est un composé ou un polymère contenant au moins deux groupes oléfiniques doublement activés de formule :

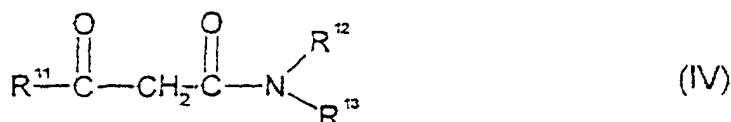


où R⁷ est un groupe capteur d'électrons, R⁸ et R⁹ sont chacun indépendamment sélectionnés à partir de l'hydrogène, d'un alkyle, qui est éventuellement substitué, et d'un aryle, qui est éventuellement substitué, X² est un -O- ou un groupe



où R¹⁰ est un hydrogène ou un groupe alkyle ; et A² est un groupe alkylène éventuellement substitué reliant le groupe oléfinique doublement activé au composé ou polymère (A) ; et dans lequel le groupe nucléophile du donneur de Michael (B) sont

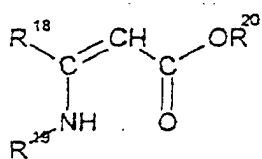
- (i) des groupes bêta-cétoamide de formule



où au moins l'un des groupes R¹¹, R¹² et R¹³ est un radical alkylène ou arylène éventuellement substitué par lequel le groupe cétoamide est lié au composé ou polymère (B) et les groupes restants R¹¹, R¹² et R¹³ sont dans le cas de R¹¹ un groupe alkyle ou aryle éventuellement substitué et dans le cas de R¹² et R¹³ un atome d'hydrogène ou un groupe alkyle ou aryle éventuellement substitué, à condition qu'au moins l'un des groupes

R¹² ou R¹³ soit différent d'un aryle ou arylène, ou
 (ii) des groupes énamine bêta-carboxylate de formule

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(VI)

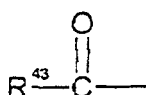
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où au moins l'un des groupes R¹⁸, R¹⁹ et R²⁰ est un radical alkylène éventuellement substitué ou R¹⁸ est un radical arylène éventuellement substitué, par lequel le groupe énamine carboxylate est lié au composé ou polymère (B) et des groupes restants R¹⁸ est un atome d'hydrogène ou un groupe alkyle ou aryle éventuellement substitué, R¹⁹ est un atome d'hydrogène ou un groupe alkyle éventuellement substitué et R²⁰ est un groupe alkyle éventuellement substitué.

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11. Composition de revêtement, d'adhésif ou de produit d'étanchéité selon la revendication 10, **caractérisée en ce que** les groupes capteurs d'électrons de l'accepteur de Michael (A) sont sélectionnés à partir de -CN, groupes acyles de formule

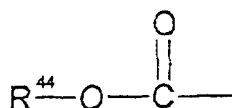
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où R⁴³ est un groupe alkyle ou aryle éventuellement substitué, des groupes ester de formule

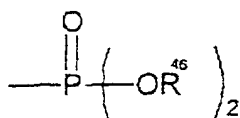
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où R⁴⁴ est un groupe alkyle ou aryle éventuellement substitué, des groupes amide de formule -CON(R⁴⁵)₂ où chaque groupe R⁴⁵, qui peut être le même ou différent, est sélectionné à partir de l'hydrogène et de groupes alkyle ou aryle éventuellement substitués et de groupes ester de phosphate de formule

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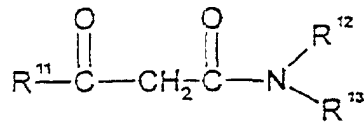
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où R⁴⁶ est un groupe alkyle ou aryle éventuellement substitué.

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12. Composition de revêtement, d'adhésif ou de produit d'étanchéité selon la revendication 9 ou 10, **caractérisée en ce que** les groupes nucléophiles du donneur d'électrons (B) sont des groupes bêta-cétoamide de formule

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(IV)

comme défini dans la revendication 10.

13. Composition de revêtement, d'adhésif ou de produit d'étanchéité selon l'une quelconque des revendications 1 à 12, contenant un catalyseur amine tertiaire, **caractérisée en ce que** le catalyseur est une amine tertiaire à encombrement stérique capable d'agir comme un stabilisateur de lumière.