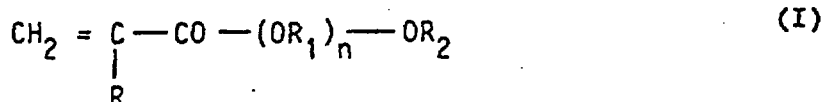


Case 154-0136

NEW VINYL ESTERS AND THEIR USE IN THE BUILDING INDUSTRY

According to the invention there is provided a composition comprising

a) one or more compounds of formula I

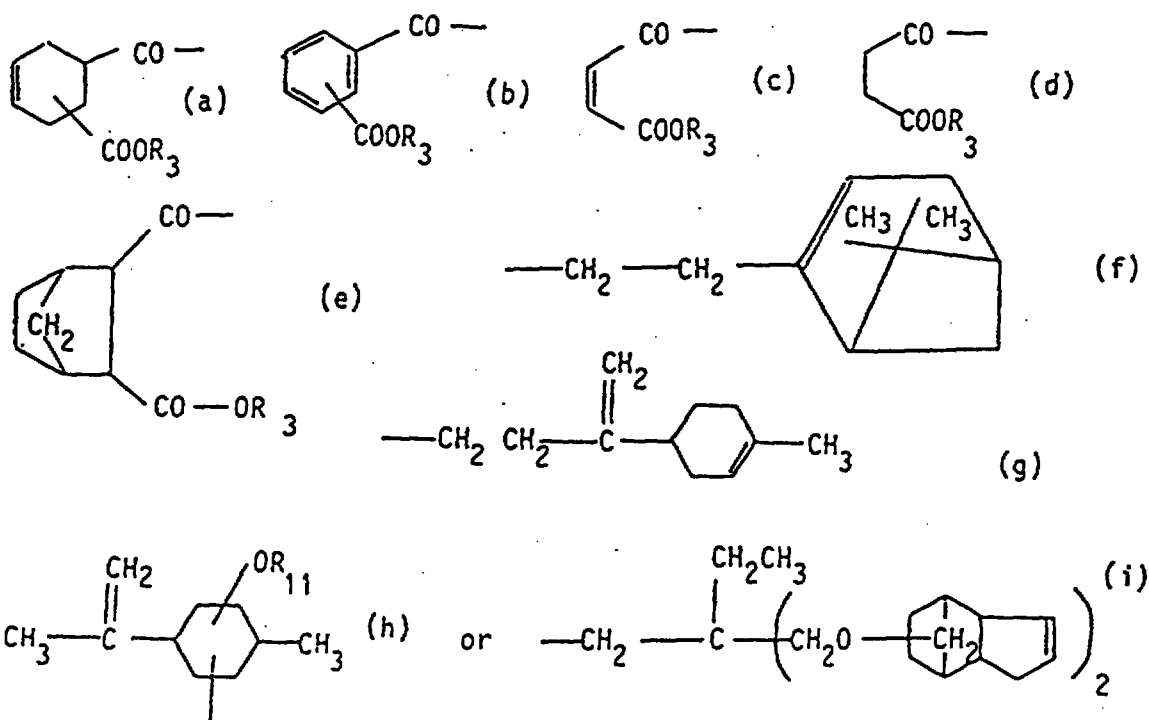


in which R is hydrogen or methyl,

R₁ is linear or branched C₂₋₈ alkylene

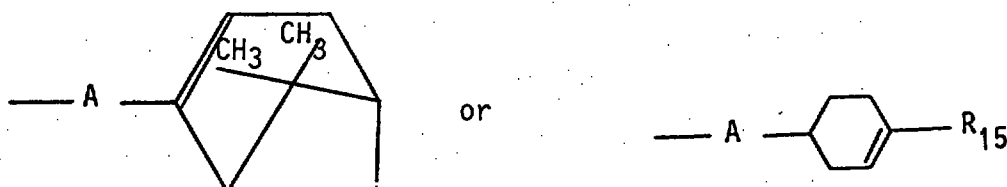
n is an integer from 1 to 10 inclusive

R₂ is a group of formula a) to i)



where R₃ is a linear or branched C₁₋₂₂ alkyl group, linear or branched C₂₋₂₂ alkenyl, unsaturated or saturated C₅₋₆ cycloalkyl (e.g.

cyclohexyl or cyclopentyl), phenyl, naphthyl,



where A is C₁₋₆ alkylene or C₂₋₆ alkenylene; R₁₁ is hydrogen or acetyl; and R₁₅ is C₁₋₆ alkyl; (hereinafter referred to as component a) and

b) optionally one or more vinyl compounds that are other than of formula I (hereinafter referred to as component b); and

c) 0.1 to 10 % (based on the weight of components a) and b) present) of two or more polymerisation catalysts (hereinafter referred to as component c), all percentages being by weight of the composition.

Preferably 20-100, more preferably 50-95 % of component a) and 0 to 80, more preferably 5-50 % of component b) based on the total weight of monomers are present in a composition according to the invention.

Compositions according to the invention preferably contain

d) 40-95 % based on the total weight of the composition of inorganic aggregate (hereinafter referred to as component d).

The addition of the polymerisation catalysts (component c), for example, organic hydroperoxide and aromatic amine accelerator and optionally a polyvalent metal salt complex can be made to the monomer mixture prior to application. The proportion of metal salt or complex added to the composition before application may be from 0.0005 weight percent up to about 2 weight percent, and the amount of hydroperoxide

may be in the range of 0.1 to 5 weight percent, based on the total weight of the monomers. Similarly, the addition of an organic peroxide, with an aromatic amine accelerator; and optionally with a polyvalent metal salt or complex, can be made to the mixture prior to application. The proportion of the organic peroxide to the composition may be in the range of 0.1 to 5 weight percent and the aromatic amine accelerator is used in an effective amount, usually in the range of about 0.1 to 5 weight percent.

The polymerisation catalyst components, such as polyvalent metal salt or complex and hydroperoxide, and amine accelerator or the aromatic amine accelerator and peroxide, may be packed and shipped separately to the site of operations where the respective components may be combined and where the composition of the present invention is to be applied, as by pouring or spraying to impregnate or seal a concrete floor or base or pavement. Alternatively, the aromatic amine accelerator and binder monomer system, and the organic peroxide (optionally together with aggregate) respectively, may be combined in packages for storing and shipping prior to combining them to provide the composition of the invention shortly before applying the composition.

The polyvalent metal salt or complex used in the invention may be any polyvalent metal-containing salt that catalyzes the oxidative curing of drying oils and, when added to oil-based varnishes and paints, hastens the drying or curing thereof. These metal salts or complexes are also known, in the art, as "siccatives" or "driers". Such substances include the polyvalent metal salts of higher aliphatic having from 8 to 30 carbon atoms or of naphthenic acids that provide solubility in the binder monomer system. Generally, the most useful drier salts for the compositions of the present invention are salts of naphthenic acids or of C₈₋₃₀ aliphatic acids. Examples of the polyvalent metal include calcium, copper ^{II}, zinc ^{II}, manganese ^{II}, manganese ^{III}, lead ^{II}, cobalt ^{II}, iron ^{III}, vanadium ^{II} and zirconium ^{IV}. These salts or complexes accelerate the action of the organic hydroperoxide and promote oxidative curing in the organic peroxide-amine catalyst system. Other examples of the acid component

or anion of the drier salt are those of resinic acids, 2-ethylhexanoic acid, lauric acid, palmitic acid, myristic acid, stearic acid, oleic acid, linoleic acid, behenic acid, cerotic acid, monotanic acid and abietic acid. A mixture of drier salts may be used.

Preferred drier salts are those of cobalt and manganese, such as cobalt octoate, cobalt naphthenate, cobalt acetylacetonate and manganese octoate, manganese naphthenate, and manganese acetylacetonate.

Aromatic amines may be used in small amounts with the organic peroxides and generally accelerate the action of the peroxide. For example, aniline, N,N-dimethylaniline, N,N-diethylaniline, toluidine, N,N-dimethyl p-toluidine, N,N-di(hydroxyethyl)toluidine, and p-dimethylaminobenzaldehyde may be added for this purpose in an amount of 0.1 to 2 percent by weight of the binder monomer system.

The organic peroxides and hydroperoxides that may be used include the peroxides and the hydroperoxides derived from hydrocarbons which contain from about 3 to 18 carbon atoms so that they are soluble in the binder monomer system. Suitable organic hydroperoxides include tertiary-butylhydroperoxide, cumene hydroperoxide, methyl ethyl ketone hydroperoxide and diisopropylbenzene hydroperoxide. Suitable peroxides include benzoyl peroxide, tert-butylperbenzoate, dilaurylperoxide, di-(4-tert.butyl-cyclohexyl)-peroxide dicarbonate, 2,2-bis-(tert-butylperoxy)-butane, bis-(1-hydroxy-cyclohexyl)-peroxide, and tert-butylperoxy-isopropyl carbonate.

A preferable polymerization catalyst is a mixture of an organic peroxide and an aromatic amine. A more preferable polymerization catalyst is a mixture of benzoyl peroxide or cumene hydroperoxide and N,N-dimethyl p-toluidine. An especially preferred polymerization catalyst is a mixture of p-dimethylaminobenzaldehyde, benzoyl peroxide or cumene hydroperoxide and cobalt naphthenate.

The aggregate material (component d) optionally used herein may be

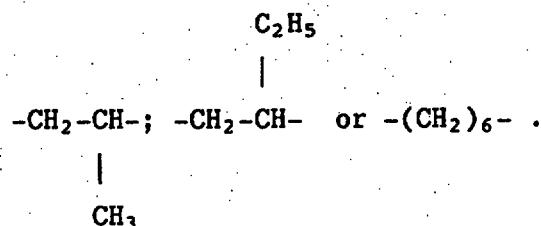
any inert inorganic substance that is resistant to such organic and inorganic acids, salts and alkalis as may be encountered in common industrial plants, e.g. hydrochloric acid, sulfuric acid, nitric acid, sulfonic acid, phosphoric acid, acetic acid, formic acid; and sodium, potassium, calcium and magnesium salts, e.g. the chlorides, sulfates and alkali metal and alkaline earth metal hydroxides. Examples of suitable aggregates include sand, silica flour, crushed rocks or stones of quartz, granite, feldspar, gneiss, basalt, porphyry, and small pebbles thereof. The sand that may be used may be of any quality or of any size. Graded sand of medium particle size such as "Ottawa" sand and "Best" sand or a mixture of the two may be used to better advantage. Ottawa sand is a silica sand of the type referred to as "round". Best sand is of the type known as "sharp". In both cases, fines will have been removed. In general, however, the sieve size of the sand may vary over a fairly wide range. In lieu of or in addition to sand, it is possible to use fractured colored glass marbles, ground glass, silica flour, emery powder, ground slag, and fine gravel.

Further according to the invention there is provided a three package composition, adapted to be used together,

- a first package comprising components a) and b)
- a second package comprising component c) and,
- a third package comprising component d).

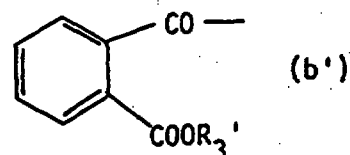
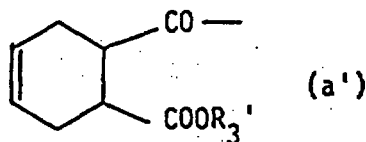
The second and third packages may also be combined together or the first and third packages may be combined together.

Preferably R_1 is R_1' where R_1' is $-\text{CH}_2-\text{CH}_2-$;



Preferably n is 1.

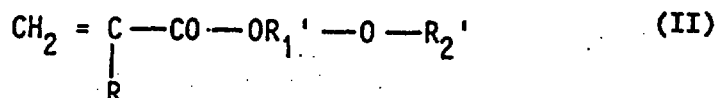
Preferably R_2 is R_2' where R_2' is a group of formula a' or b'



where R_3' is as defined below.

Preferably R_3 is R_3' where R_3' is a linear or branched C_{1-12} alkyl or C_{2-12} alkenyl.

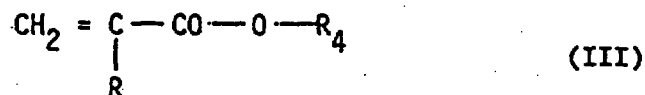
Preferably in a composition according to the invention, the compounds of formula I are those of formula II



where the symbols are as defined above.

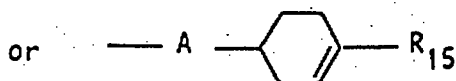
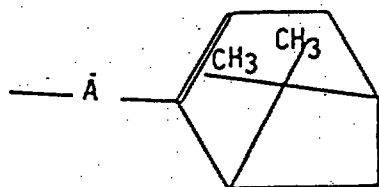
Preferably component b), when present, is

i) a compound of formula III



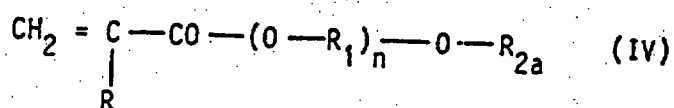
in which R is as defined above and,

R_4 is linear or branched C_{1-22} alkyl, unsubstituted or substituted by one or more (preferably 1 to 3) groups selected from hydroxy, carboxy, thio or an amide group or R_4 is C_{3-6} cycloalkyl, phenyl, naphthyl,

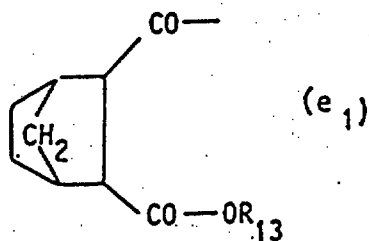
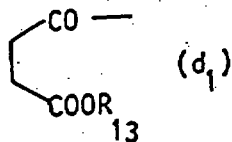
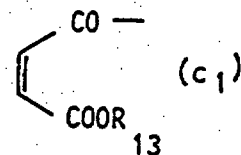
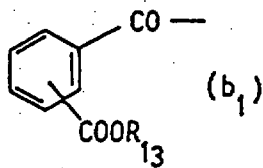
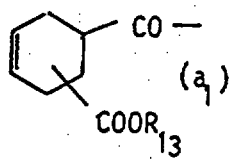


where A and R_{15} are as defined above; or

ii) a compound of formula IV



in which R, R_1 and n are as defined above and R_{2a} is a group of a_1 to e_1



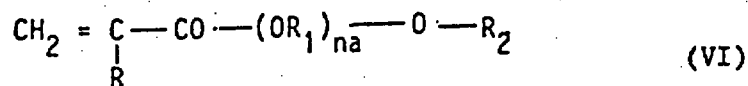
where R_{13} is hydrogen, an alkali or alkaline earth metal cation or a mono-, di- or tri- C_1 -s alkylamine, unsubstituted or substituted by 1 to 3 OH groups.

Preferably component c) is

a combination of 0.1 to 5 % by weight C_{3-18} hydrocarbyl peroxides or C_{3-18} hydrocarbyl hydroperoxides and 0.005-2 % by weight of a polyvalent metal salt or a complex and/or 0.1 to 5 % of an aromatic amino group containing polymer accelerator,

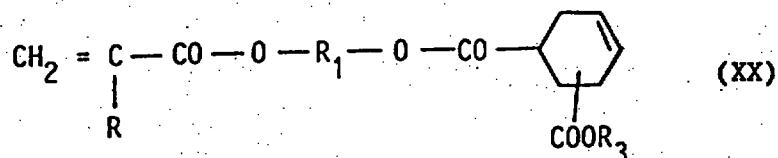
all percentages being based on the weight of components a) and b) present.

Further according to the invention there is provided a compound of formula VI



where na is an integer of from 2 to 10 inclusive and the other symbols are as defined above.

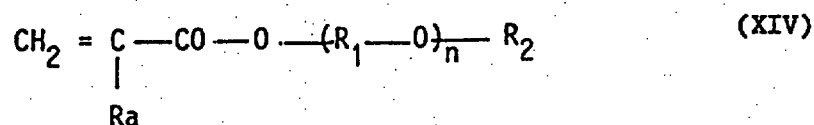
Further according to the invention there is provided a compound of formula XX



in which the symbols are as defined above.

Further according to the invention there is provided a compound of formula V as defined above.

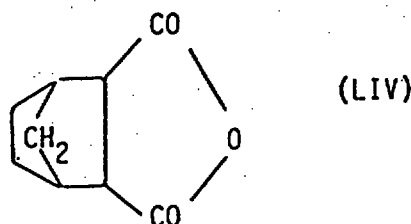
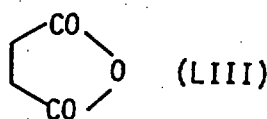
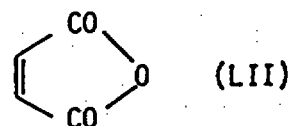
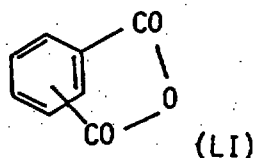
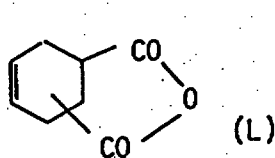
Further according to the invention there is provided a compound of formula XIV



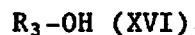
in which R_a is methyl and R_3 is other than C_{10-18} alkyl and the other symbols are as defined above.

Compounds of formula I where R_2 is a group of formula a) to e) can be formed by

i) reacting 1 mole of an anhydride of one of formulae L to LIV



with 1 mole of a compound of formula XVI

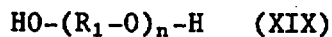


at an elevated temperature to form a compound of formula XVII

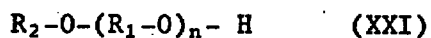


followed by

ii) reacting 1 mole of a compound of formula XVII with 1 mole of a compound of formula XIX



at an elevated temperature to form a compound of formula XXI



where R_2 is as defined above

followed by

iii) reacting 1 mole of a compound of formula XXI with 1 mole of a compound of formula XXII



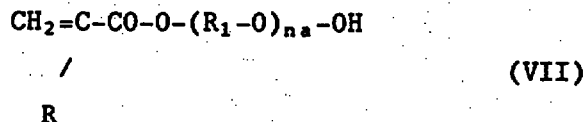
at an elevated temperature to form a compound of formula I.

In the above reactions, elevated temperature means a temperature from 40-110°C.

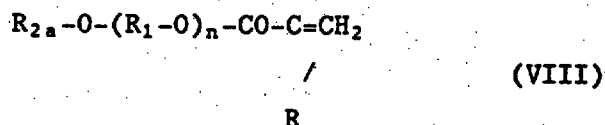
A compound of formula VI where R_3 is not alkenyl can be prepared

by

a) reacting 1 mole of a compound of formula VII



with 1 mole of an acid anhydride of formula L to LV above to form a compound of formula VIII



in which the symbols are as defined above, at an elevated temperature, the compound of formula VIII optionally being salted by reaction with alkali to form an alkali metal salt; followed by

b) reacting 1 mole of the compound of formula VIII or a salt thereof with 1 mole of a compound of formula IX



where A_1 is a group capable of being split off from R_3 , at elevated temperature.

Other compounds of formula I can be made by known methods from known compounds.

Preferred compounds of formula IX are $\text{R}_3 - \text{O} - \text{SO} - \text{Cl}$, C_{1-4} alkyl or cyclohexyl-chloro sulphites, di- R_3 -sulphates, tri- R_3 -phosphates, tri- R_3 -phosphites or R_3 -halogen (in a suitable solvent such as hexamethyl phosphoric acid triamide). Reaction b can also be carried out in the presence of isonitrile and Cu_2O .

Preferably the elevated temperature of reaction a) is 80-110°C and

for reaction b) is 40-60°C.

Compounds of formula XX can be made by an analogous method using a compound of formula VII where n_a is 1 and a compound of formula VIII where R_{2a} is a group of formula a_1 .

Compounds of formula XIV can be prepared by reacting a compound of formula VII where n_a is n and R is methyl with an anhydride of formula L to LIV followed by reacting the product with a compound of formula IX.

Compounds of formula I when $n=1$ and R_{2a} is derived from acrylic acid are known or can be made from known compounds by known methods.

Methyl esters of compounds of formula I (e.g. where R_3 is methyl) can be reacted with linear or branched fatty alcohols to form appropriate fatty alcohol esters by known methods (eg. in the presence of alkali catalysts).

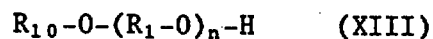
Compounds of formula III can be prepared by known methods from appropriate reactants.

Compounds of formula IV can be made by a method analogous to that for forming compounds of formula I from appropriate reactants.

Compounds of formula V can be prepared by reacting 1 mole of a compound of formula XII

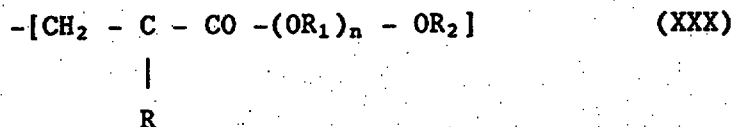


with 1 mole of a compound of formula XIII



where the symbols are as defined above, at an elevated temperature (e.g. at 40-60°C).

Further according to the invention there is provided a homo- or co-polymer containing at least 3 recurring units of formula XXX



in which the symbols are as defined above optionally together with 40-90% (based on the weight of the total composition) of component d).

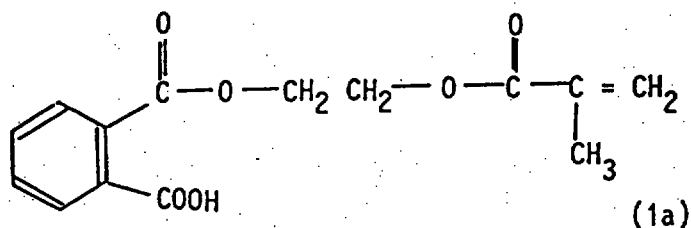
Preferably the number of recurring units of formula XXX is from 3 to 50 inclusive.

Compositions according to the invention containing components a), [optionally b)], c) and d) are useful for repairing concrete materials or surfaces. Such a composition is applied to the surface requiring repair and is allowed to harden at ambient temperatures.

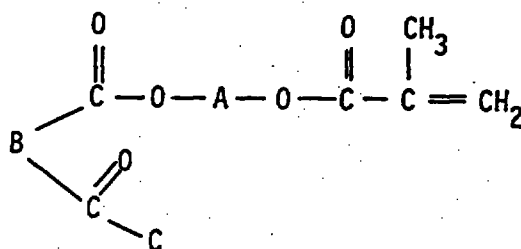
The compositions or compounds according to the invention can be used alone or together with filler for impregnating and/or covering porous material, especially concrete, for example for filling cracks. Such uses described in US Patent 4,460,625.

Examples 1 to 6

1 mole of phthalic acid anhydride is reacted with 1 mole of methacrylic acid glycolester at a temperature of about 100° to form an intermediate of formula 1a.



The compound of formula 1_a is neutralised with sodium hydroxide and reacted at 40° with ½ mole of dimethyl sulphate. The resulting compound of formula 1 defined below is a liquid, with a viscosity, measured in a Brookfield viscosimeter, Spindle 2 at 60 rpm as given in the Table below. By an analogous method further compounds of formula 1 where the symbols are defined in the Table can be obtained from appropriate reactants.



Table

Example	A	B	C	Viscosity
1	ethylene	o-phenylene	methyl	60
2	ethylene	o-phenylene	isononyl	380
3	ethylene	o-phenylene	isopentyl	246
4	ethylene	o-tetrahydro- phenylene	methyl	65±4
5	propylene	o-tetrahydro- phenylene	methyl	66±3
6	propylene	o-phenylene	methyl	56

Application Example

The compound of formula 1 of example 1 and the intermediate of formula 1_a are mixed with aggregate and catalysts according to the following recipe.

sand	229.2 g
silica fume	23.2 g

compound of formula 1 of Ex 1	42.75g
compound of formula 1 _a	2.25g
dimethylaminobenzaldehyde	1.8 g
cumenehydroperoxide	0.9 g
cobalt naphthenate	0.9 g

	300 g

This composition hardens within 15 minutes and can be tested for strength after 12 hours. For dispatch to the building site, the aggregate, the monomer and the catalyst composition are packed in different packages.

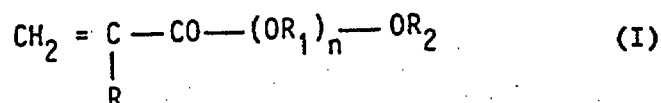
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Claims

1. A composition comprising

a) one or more compounds of formula I

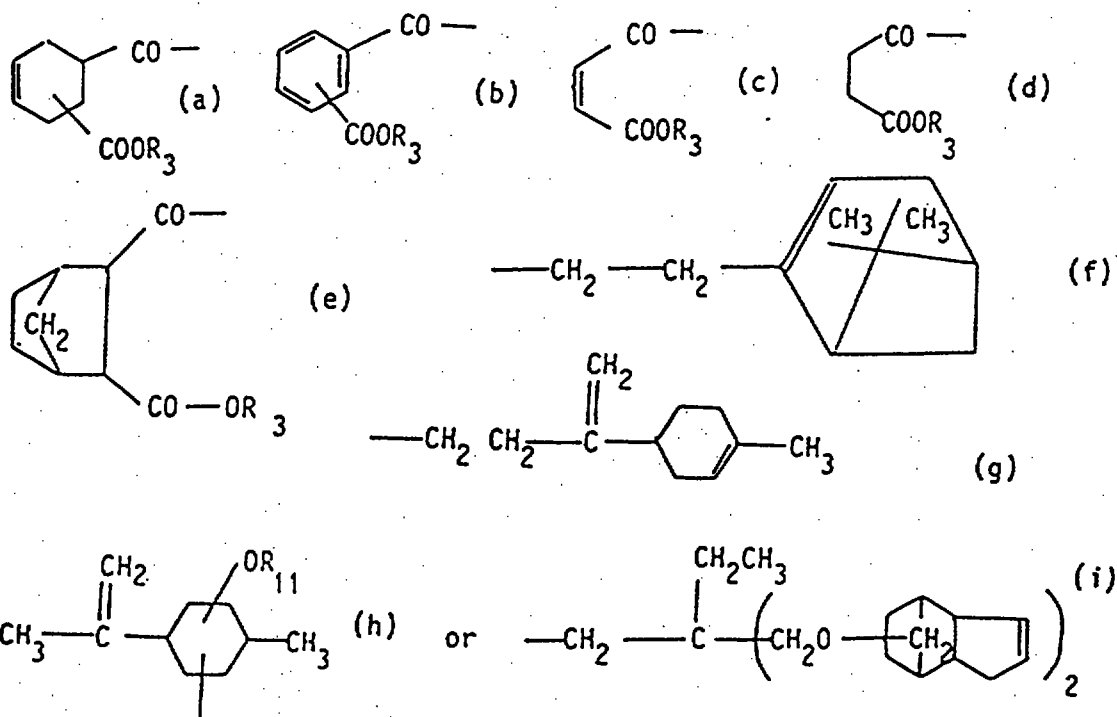


in which R is hydrogen or methyl,

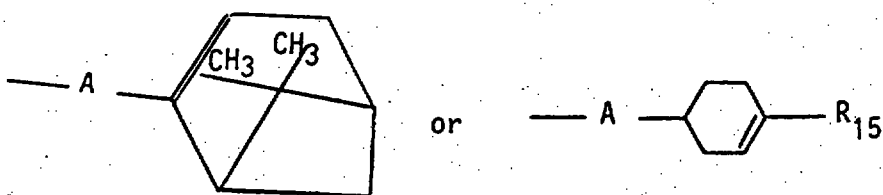
R₁ is linear or branched C₂₋₈ alkylene

n is an integer from 1 to 10 inclusive

R₂ is a group of formula a) to i)



where R₃ is a linear or branched C₁₋₂₂ alkyl group, linear or branched C₂₋₂₂ alkenyl, unsaturated or saturated C₅₋₆ cycloalkyl (e.g. cyclohexyl or cyclopentyl), phenyl, naphthyl,



where A is C₁₋₆ alkylene or C₂₋₆ alkenylene; R₁₁ is hydrogen or acetyl; and R₁₅ is C₁₋₆ alkyl; (hereinafter referred to as component a) and

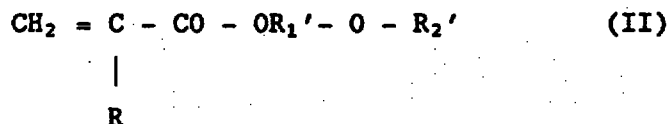
b) optionally one or more vinyl compounds that are other than of formula I (hereinafter referred to as component b); and

c) 0.1 to 10 % (based on the weight of components a) and b) present) of two or more polymerisation catalysts (hereinafter referred to as component c), all percentages being by weight of the composition.

2. A composition according to Claim 1 containing 20 to 100% of component a) and 0 to 80% of component b).

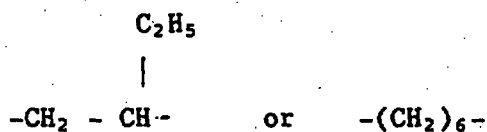
3. A composition according to Claim 1 or Claim 2 containing 40-95% based on the total weight of composition of inorganic aggregate.

4. A composition according to any one of the preceding claims in which compound a) is a compound of formula II

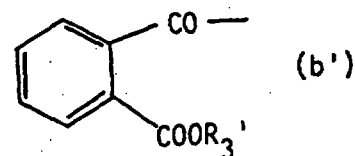
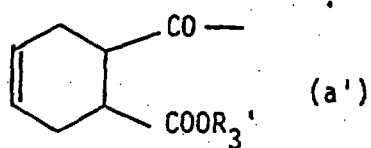


where R₁' is -CH₂ - CH₂-; -CH₂ - CH-;





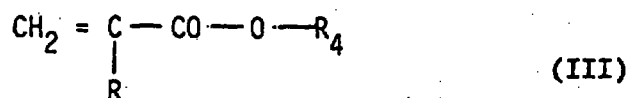
R₂' is a group of formula a' or b'



where R₃' is a linear or branched C₁₋₁₂ alkyl or C₂₋₁₂ alkenyl group; and R is hydrogen or methyl.

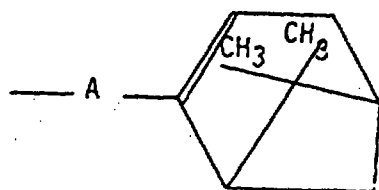
5. A composition according to any one of the preceding claims in which component b) is selected from

i) a compound of formula III

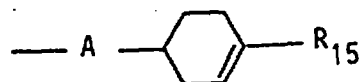


in which R is as defined above and,

R₄ is linear or branched C₁₋₂₂ alkyl, unsubstituted or substituted by one or more (preferably 1 to 3) groups selected from hydroxy, carboxy, thio or an amide group or R₄ is C₅₋₆ cycloalkyl, phenyl, naphthyl,



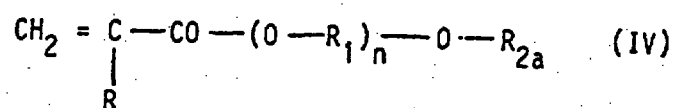
or





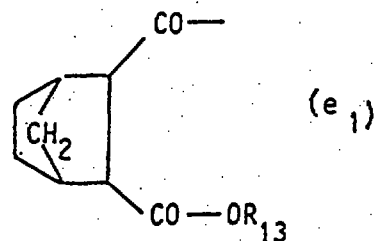
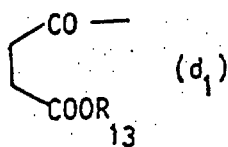
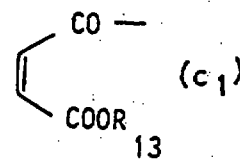
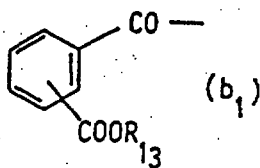
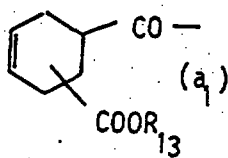
where A and R₁₅ are as defined in claim 1; and

ii) a compound of formula IV



in which R, R₁ and n are as defined in Claim 1;

R_{2a} is a group of a₁ to e₁



where R₁₃ is hydrogen, an alkali or alkaline earth metal cation or a mono-, di- or tri- C₁₋₃ alkylamine, unsubstituted or substituted by 1 to 3 OH groups,

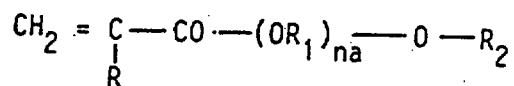


6. A composition according to Claim 1 in which component c) is

a combination of 0.1 to 5 % by weight C_{3-18} hydrocarbyl peroxides or C_{3-18} hydrocarbyl hydroperoxides and 0.005-2 % by weight of a polyvalent metal salt or a complex and/or 0.1 to 5 % of an aromatic amino group containing polymer accelerator,

all percentages being based on the weight of components a) and b) present.

7. A compound of formula VI



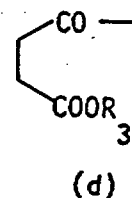
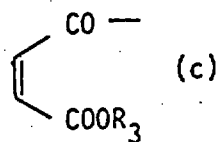
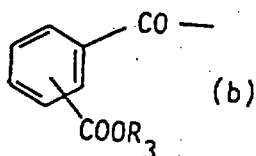
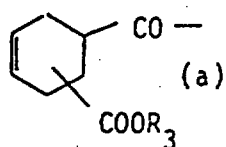
(VI)

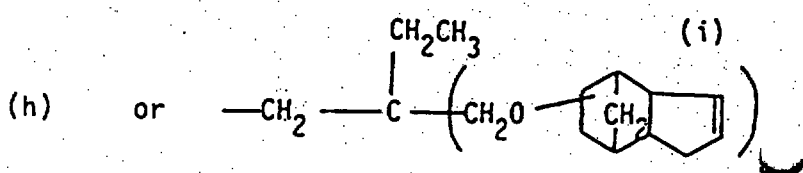
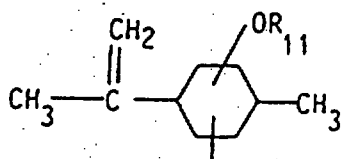
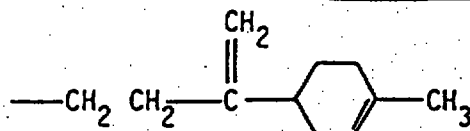
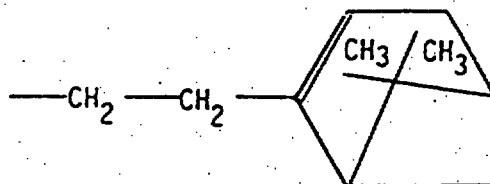
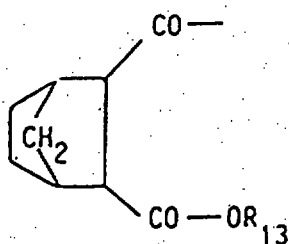
in which R is hydrogen or methyl

R_1 is linear or branched C_{2-8} alkylene

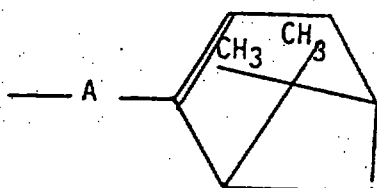
na is an integer of from 2 to 10 inclusive;

R_2 is a group of formula a) to i)

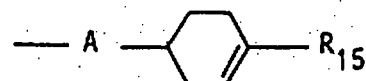




where R_3 is a linear or branched C_{1-22} alkyl group, linear or branched C_{2-22} alkenyl, unsaturated or saturated C_{5-6} cycloalkyl (e.g. cyclohexyl or cyclopentyl), phenyl, naphthyl,

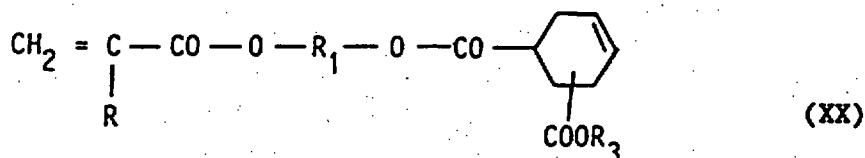


or



where A is C_{1-6} alkylene or C_{2-6} alkenylene; R_{11} is hydrogen or acetyl; and R_{15} is C_{1-6} alkyl.

8. A compound of formula XX



in which R is hydrogen or methyl

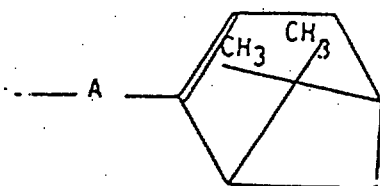
R_1 is linear or branched C_{2-8} alkylene

where R_3 is a linear or branched C_{1-22} alkyl group, linear or branched C_{2-22} alkenyl, unsaturated or saturated C_{5-6} cycloalkyl (e.g. cyclohexyl or cyclopentyl), phenyl, naphthyl,

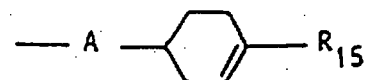


-22-

Case 154-0136

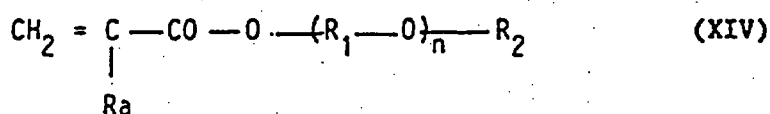


or



where A is C₁₋₆ alkylene or C₂₋₆ alkenylene; R₁₁ is hydrogen or acetyl; and R₁₅ is C₁₋₆ alkyl.

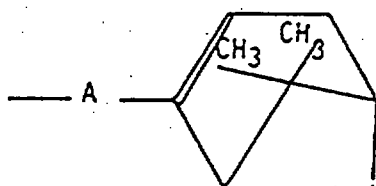
9. A compound of formula XIV



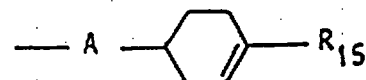
in which R₁, R₂ and n are as defined in claim 1;

R₄ is methyl;

R₃ is a linear or branched C₁₋₂₂ alkyl group, linear or branched C₂₋₂₂ alkenyl, unsaturated or saturated C₃₋₆ cycloalkyl (e.g. cyclohexyl or cyclopentyl), phenyl, naphthyl,



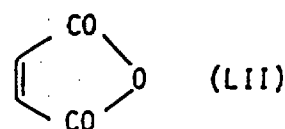
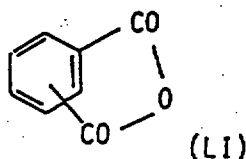
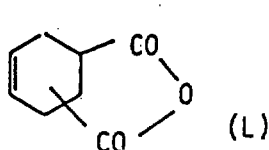
or

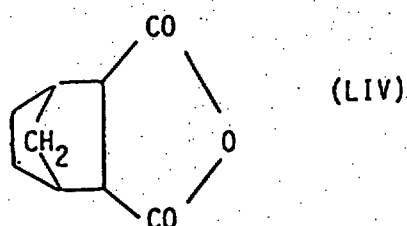
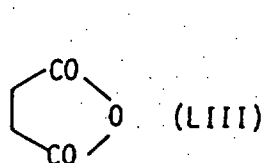


where A as C₁₋₆ alkylene or C₂₋₆ alkenylene; R₁₁ is hydrogen or acetyl and R₁₅ is C₁₋₆ alkyl; with the proviso that R₃ is other than C₁₀₋₁₈ alkyl.

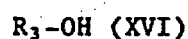
10. A process for preparing a compound of formula I according to Claim 1 where R₂ is a group of formula a) to e) comprising

i) reacting 1 mole of an anhydride of one of formulae L to LIV

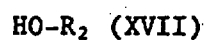




with 1 mole of a compound of formula XVI

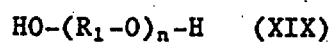


at an elevated temperature to form a compound of formula XVII



followed by

ii) reacting 1 mole of a compound of formula XVII with 1 mole of a compound of formula XIX



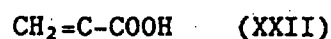
at an elevated temperature to form a compound of formula XXI



where R_2 is as defined above

followed by

iii) reacting 1 mole of a compound of formula XXI with 1 mole of a compound of formula XXII



R



at an elevated temperature to form a compound of formula I.

11. A compound of formula I substantially as herein described with reference to any one of Examples 1 to 6.

12. A composition substantially as herein described with reference to the Application Example.
