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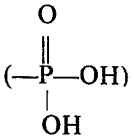
SHIBATANI and TOORU WADA

(54) ADHESIVE CEMENTING AGENTS CONTAINING PARTIAL PHOSPHORIC OR PHOSPHONIC ACID ESTERS

(71) We, KURARAY CO. LTD., a Japanese body corporate, of 1621, Sakazu, Kurashiki-city, Japan, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to adhesive cementing agents for the hard tissues of the human body, including the tooth and bones. More particularly, the invention relates to adhesive cementing agents of the type in which an intimate bonding affinity for human tissues is desired, such as cements for the treatment of a complex fracture of bone or for fixation of artificial joints, dental adhesives, dental fillers and dental restorative.

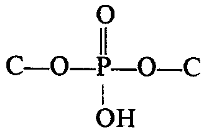
In the conventional dental filling agents of the cold-cure type (curable at room temperature), as well as in cementing agents for the fixation of artificial joints, a mixture of polymethyl methacrylate and methyl methacrylate or a mixture of bisphenol-A diglycidyl dimethacrylate and triethylene glycol dimethacrylate, among other combinations, is used and allowed to cure *in situ* in the presence or absence of an inorganic filler and mainly by means of a peroxide-amine catalyst system that generates free radicals. The cured composition obtainable by this known method has substantially no bonding affinity for tissues (except for acid-treated dental enamel), the bonding strength under wet conditions being as low as about 0 to 5 kg/cm². For this reason, in conventional filling practice, e.g. for the treatment caries, mechanical retainer means known as undercuts have heretofore been applied to the cavity to lock the cured filling agent in position. This procedure, however, is disadvantageous in that it removes a healthy portion of the tooth and in that because of the lack of bond between the filler and the tooth proper, it provides only a poor marginal seal, which often permits a relapse of tooth decay or other tissue defect. As a preventive filling agent and an orthodontial cement, both adapted to provide a sealing bond with the tooth, adhesive agents based on α-cyanoacrylate have been developed in recent years but these agents are known to be lacking in durability in the mouth as well as in handlabily. A dental-cement-filling-agent containing a trialkylboron compound as a polymerization initiator ingredient has also been developed (Japanese Patent Publication No. 14318/1967 and No. 29195/1970) but whilst it provides a firm bond with the dentin, it does not have an adequate bonding affinity for the enamel. Moreover, since the resin is primarily based on methyl methacrylate, this product is not fully satisfactory for dental filling purposes. A procedure has also been developed which employs a vinyl compound containing a divalent phosphoric acid



$$(-\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}-\mathrm{OH})$$

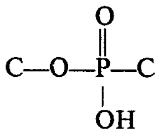
which is claimed to provide a bond with the calcium of the tooth (Japanese Patent Application laid-open No. 44152/1976; Journal of Dental Research *35*, 346). However, its low adhesive strength does not make the product sufficiently useful for most practical purposes. U.S. Patent No. 3882600 states that the addition of a small amount of an addition-polymerizable phosphoryl monofluoride to a dental cement composition results in an improved bond between the tooth and the composition. However, this product seems to be not truly safe to the pulp because of its interaction, which is conceivably due to the P—F bond contained in the product.

The present invention provides an adhesive cementing agent for the hard tissues of the human body comprising (a) a phosphoric and/or phosphonic acid ester compound containing at least one radical-polymerizable vinyl group and at least one



$$\mathrm{C}-\mathrm{O}-\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}-\mathrm{O}-\mathrm{C}$$

or

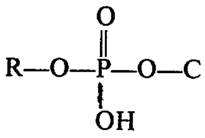


$$\mathrm{C}-\mathrm{O}-\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}-\mathrm{C}$$

bond, or a high-molecular-weight compound obtainable by polymerizing said compound either alone or as a comonomeric unit, (b) a radical-copolymerizable comonomer, preferably one comprising an acrylic or methacrylic acid ester compound, and (c) a curing agent, in which the weight of phosphorus of component (a) is not less than 0.1% of the weight of the adhesive cementing agent in actual use. Such a cementing agent may be compounded as a binder, with a filler, e.g. silica powder, aluminium powder, or quartz powder to produce a dental restorative material, and it may moreover be united with a dental filling composition comprising a filler, a monomer and a curing agent to form a dental restorative system.

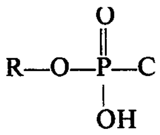
As will appear from the Examples below, the invention makes possible a cement for the hard tissues of the human body that has adequate hardness, compressive strength and other mechanical properties, adequate water-absorption characteristics, that affords a firm and lasting bond with the hard tissue of the human body, including bones and the dentin and enamel of teeth, and that is nontoxic to human beings. It is of especial value as a filling composition for teeth and as an adhesive agent for joining a dental filler to the tooth.

The phosphoric or phosphonic acid ester compound usually contains at least one



$$\mathrm{R}-\mathrm{O}-\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}-\mathrm{O}-\mathrm{C}$$

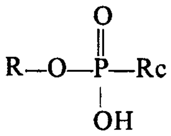
or



$$\mathrm{R}-\mathrm{O}-\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}-\mathrm{C}$$

residue, where R is an organic residue containing at least one radical-polymerizable vinyl group. The said compound is preferably one of the compounds represented by the following formulae (1) to (7).

(A) Thus, the said compound may be a compound represented by the general formula:

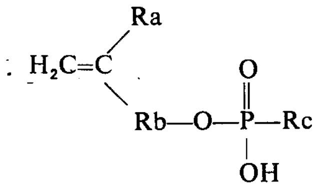


$$\mathrm{R}-\mathrm{O}-\underset{\mathrm{OH}}{\underset{|}{\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}}}-\mathrm{Rc} \qquad (1)$$

(1)

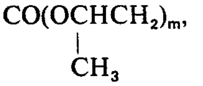
where R is an organic residue containing at least one radical-polymerizable vinyl group; Rc is X or OX where X is a straight-chain, cyclic or branched aliphatic, alicyclic or aromatic hydrocarbon residue containing 1 to 30 carbon atoms, which residue may optionally be substituted by hydroxyl, halogen, amino or carboxyl, or X is a polyether, polyester or polyurethane residue.

As a subgeneric class of compounds included in the class of phosphoric or phosphonic acid ester compounds of formula (1), there may be mentioned compounds of the following formula (2).



(2)

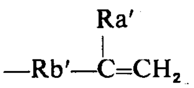
where Ra is hydrogen or methyl; Rb is COOY, OCOY, OY, Y, $CO(OCH_2CH_2)_m$,



$$CO(\underset{CH_3}{OCH}CH_2)_m,$$

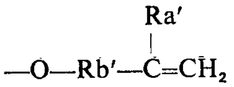
$CO(OCH_2CH_2)_k—O—C_6H_5$, where Y is a straight-chain, cyclic or branched aliphatic, aromatic or alicyclic hydrocarbon residue containing 1 to 30 carbon atoms, which residue may optionally be substituted by hydroxyl, alkoxy or halogen; Rc is as defined above and *m* is 1, 2, 3, 4 or 5 and *k* is 1, 2 or 3.

This particular subgeneric class of compounds includes the compounds in which Rc is



$$—Rb'—\overset{Ra'}{C}=CH_2$$

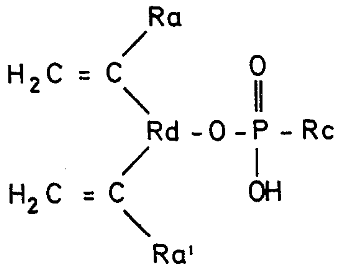
or



$$—O—Rb'—\overset{Ra'}{C}=CH_2$$

(where Ra' and Rb' are radicals of the type defined for Ra and Rb, respectively).

(B) The present compound may also be a compound of the following general formula (3):



(3)

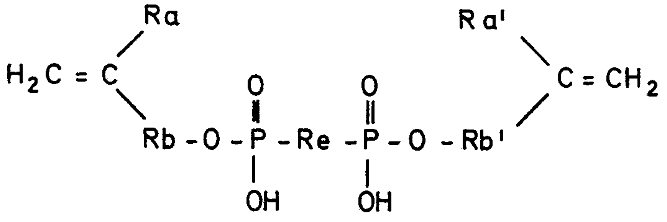
where Ra, Ra' and Rc have the meanings defined hereinbefore and Rd is

—Y—, —OY— —OYO—, —OCOY—, —OCOYO—, OCOYCOO—,

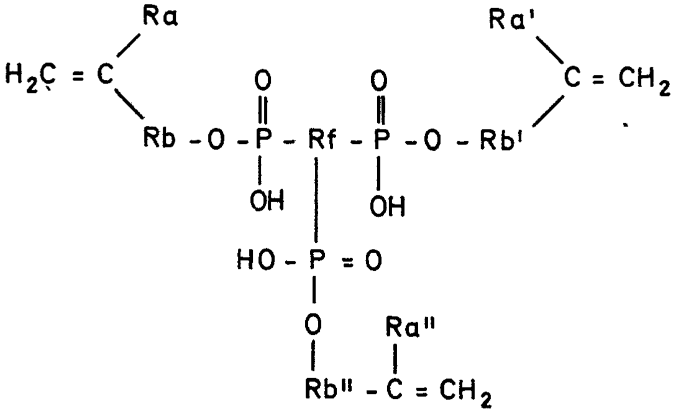
—COOY—, —COOYCOO— or —COOYOCO—,

where Y has the meaning defined hereinbefore.

(C) The present compound may be a compound of one of the following general formulae (4), (5) and (6)

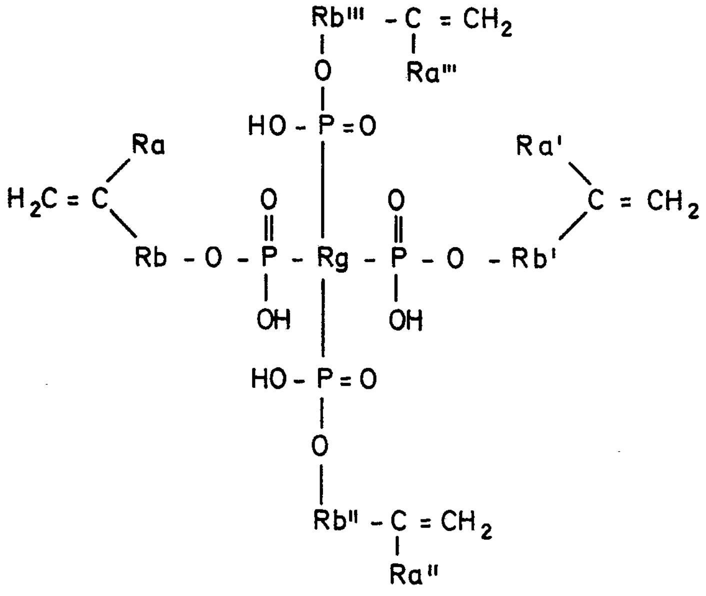


(4)



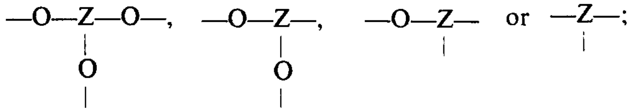
(5)

or

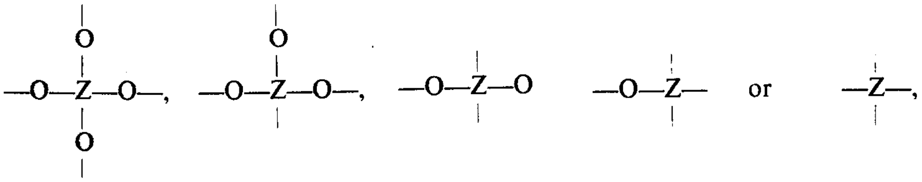


(6)

In the above formulas, Ra and Rb have the meanings hereinbefore defined; Ra', Ra'' and Ra''' are radicals of the type defined for Ra; Rb', Rb'' and Rb''' are radicals of the type defined for Rb; Re is —O—Z—O—, —O—Z— or —Z—; Rf is



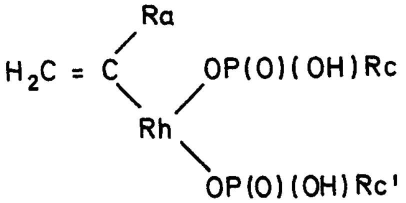
$$-\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ |}}{\mathrm{Z}}-\mathrm{O}-,\quad -\mathrm{O}-\underset{\substack{|\\ \mathrm{O}\\ |}}{\mathrm{Z}}-,\quad -\mathrm{O}-\underset{|}{\mathrm{Z}}-\ \text{or}\ -\underset{|}{\mathrm{Z}}-;$$

Rg is 

$$-\mathrm{O}-\overset{\substack{|\\ \mathrm{O}\\ |}}{\underset{\substack{|\\ \mathrm{O}\\ |}}{\mathrm{Z}}}-\mathrm{O}-,\quad -\mathrm{O}-\overset{\substack{|\\ \mathrm{O}\\ |}}{\underset{|}{\mathrm{Z}}}-\mathrm{O}-,\quad -\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Z}}}-\mathrm{O}\quad -\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Z}}}-\ \text{or}\ -\overset{|}{\underset{|}{\mathrm{Z}}}-,$$

where Z is a radical of the type defined for X.

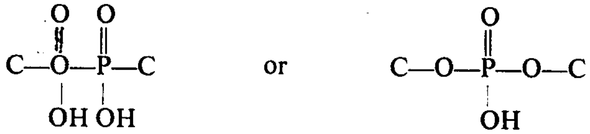
(D) The present compound may be a compound of the following general formula (7):



(7)

wherein Ra and Rc are as hereinbefore defined; Rh is COOY, OCOY, OY or Y, where Y has the same meaning as hereinbefore defined; Rc' is a radical of the type defined for Rc.

As will be apparent from the above description, the carbon atom of the P—C bond or P—O—C bond in the

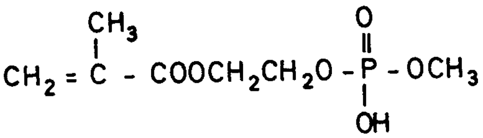


$$\mathrm{C}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{O}}}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{P}}}-\mathrm{C}\qquad \text{or}\qquad \mathrm{C}-\mathrm{O}-\overset{\overset{\mathrm{O}}{\|}}{\underset{\underset{\mathrm{OH}}{|}}{\mathrm{P}}}-\mathrm{O}-\mathrm{C}$$

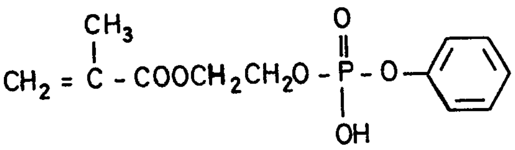
bond, as the case may be, may form a ring for the purposes of this invention.

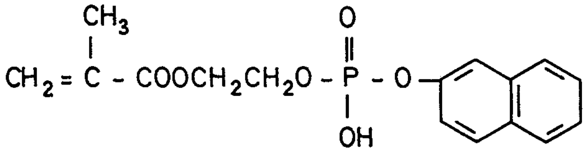
The following is a partial list of the phosphoric or phosphonic acid ester compounds used in the practice of this invention.

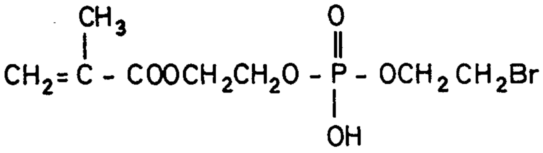
Among the compounds of formula (2):



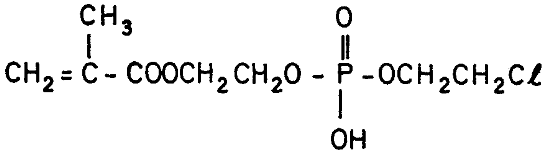
$$\mathrm{CH_2=\overset{\overset{CH_3}{|}}{C}-COOCH_2CH_2O-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OCH_3}$$



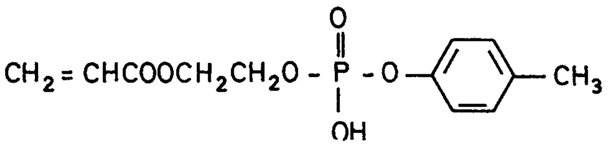


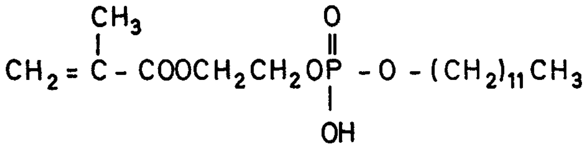


$$CH_2=\overset{CH_3}{\overset{|}{C}}-COOCH_2CH_2O-\overset{O}{\overset{\|}{\underset{\underset{OH}{|}}{P}}}-OCH_2CH_2Br$$

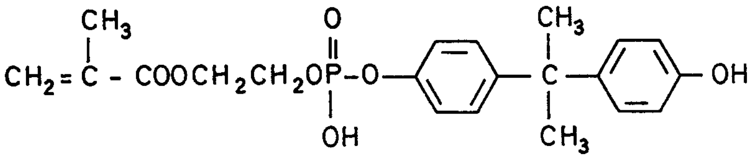


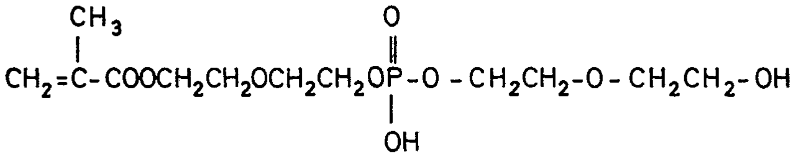
$$CH_2=\overset{CH_3}{\overset{|}{C}}-COOCH_2CH_2O-\overset{O}{\overset{\|}{\underset{\underset{OH}{|}}{P}}}-OCH_2CH_2Cl$$



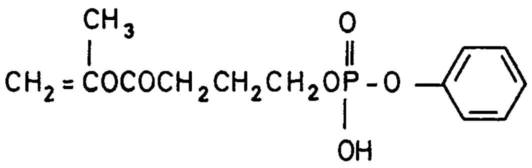


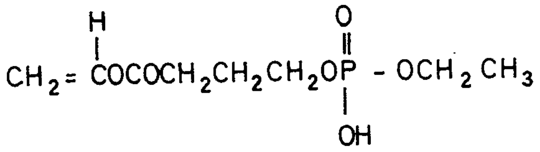
$$CH_2=\overset{CH_3}{\overset{|}{C}}-COOCH_2CH_2O\overset{O}{\overset{\|}{\underset{\underset{OH}{|}}{P}}}-O-(CH_2)_{11}CH_3$$



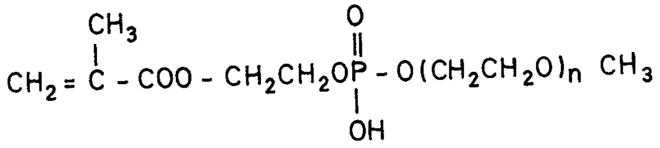


$$CH_2=\overset{CH_3}{\overset{|}{C}}-COOCH_2CH_2OCH_2CH_2O\overset{O}{\overset{\|}{\underset{\underset{OH}{|}}{P}}}-O-CH_2CH_2-O-CH_2CH_2-OH$$

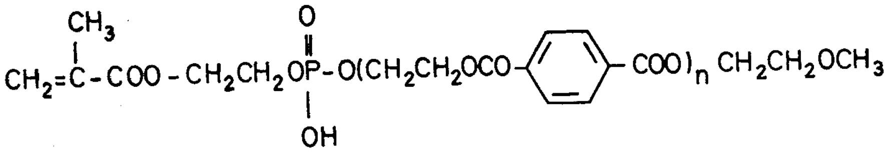


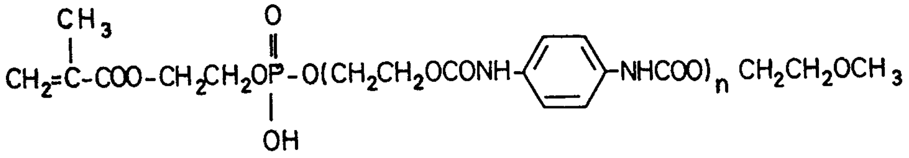


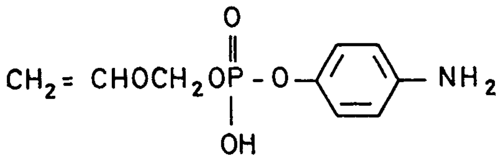
$$CH_2{=}\overset{H}{\overset{|}{C}}OCOCH_2CH_2CH_2O\overset{O}{\overset{\|}{\underset{\underset{OH}{|}}{P}}}-OCH_2CH_3$$

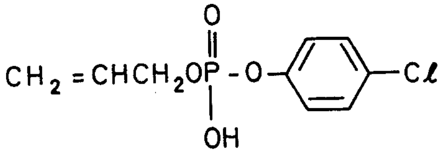


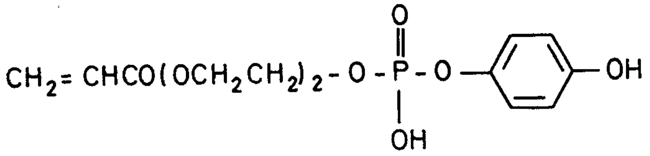
$$CH_2{=}\overset{CH_3}{\overset{|}{C}}-COO-CH_2CH_2O\overset{O}{\overset{\|}{\underset{\underset{OH}{|}}{P}}}-O(CH_2CH_2O)_n\ CH_3$$

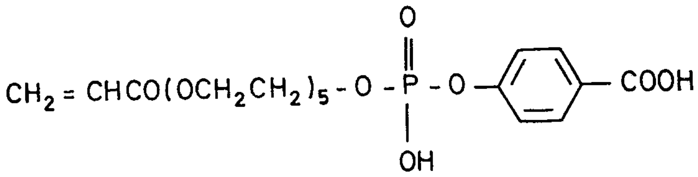


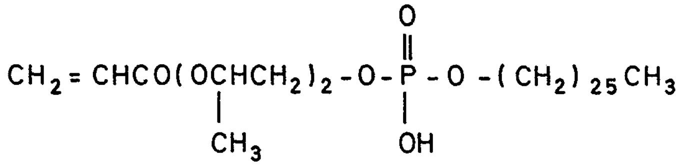




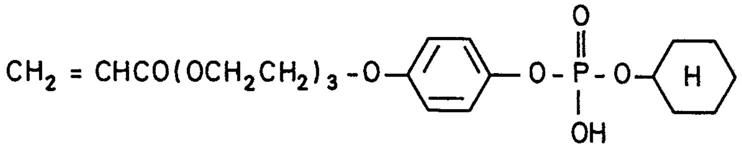


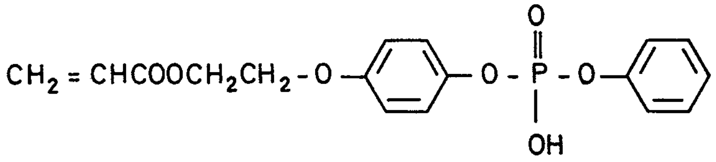


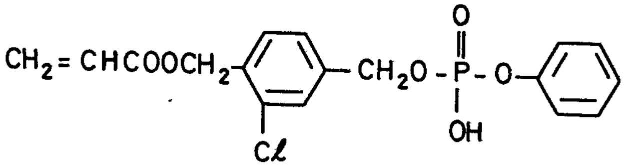


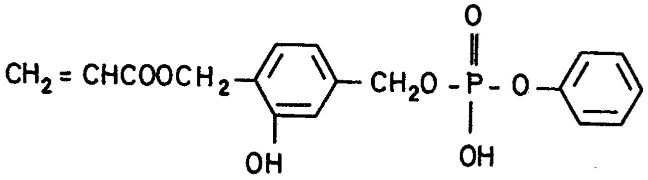


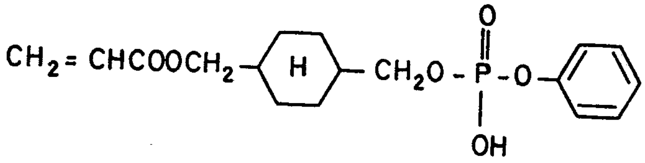
$$CH_2{=}CHCO(O\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_2)_2-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-O-(CH_2)_{25}CH_3$$

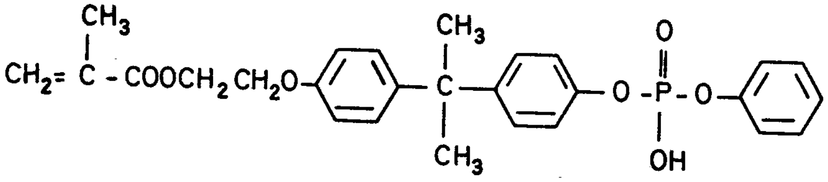


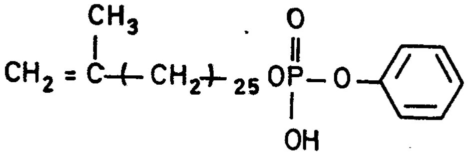


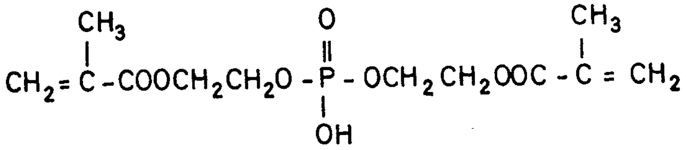




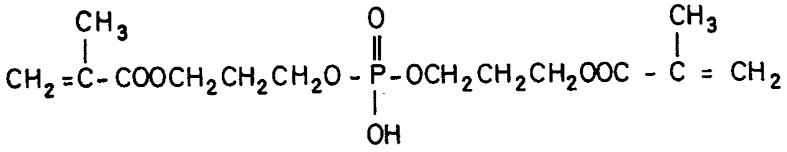




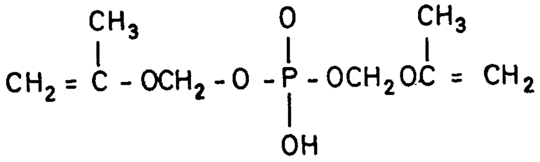




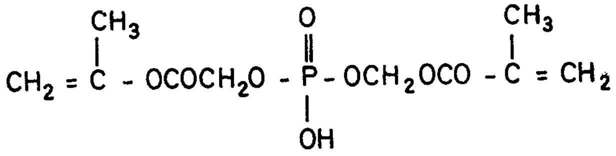
$$CH_2=\overset{CH_3}{\overset{|}{C}}-COOCH_2CH_2O-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-OCH_2CH_2OOC-\overset{CH_3}{\overset{|}{C}}=CH_2$$



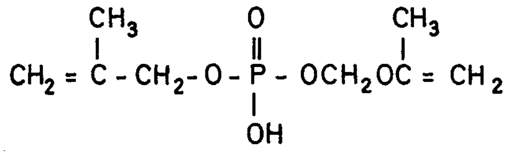
$$CH_2=\overset{CH_3}{\overset{|}{C}}-COOCH_2CH_2CH_2O-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-OCH_2CH_2CH_2OOC-\overset{CH_3}{\overset{|}{C}}=CH_2$$



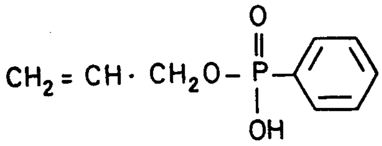
$$CH_2=\overset{CH_3}{\overset{|}{C}}-OCH_2-O-\underset{OH}{\underset{|}{\overset{O}{\overset{|}{P}}}}-OCH_2O\overset{CH_3}{\overset{|}{C}}=CH_2$$

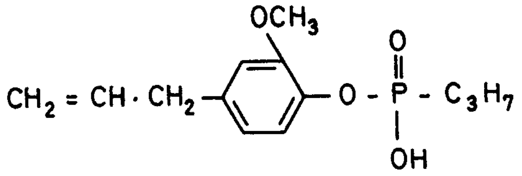


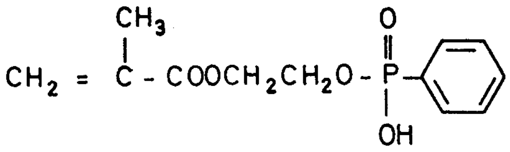
$$CH_2=\overset{CH_3}{\overset{|}{C}}-OCOCH_2O-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-OCH_2OCO-\overset{CH_3}{\overset{|}{C}}=CH_2$$

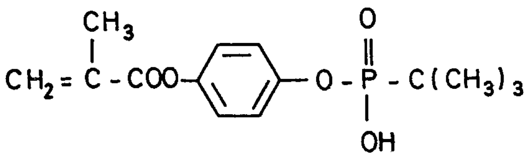


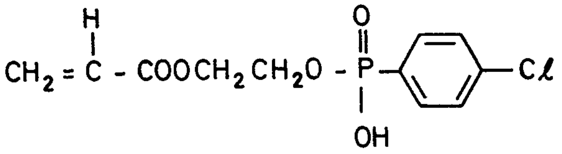
$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-O-\underset{OH}{\underset{|}{\overset{O}{\overset{\|}{P}}}}-OCH_2O\overset{CH_3}{\overset{|}{C}}=CH_2$$

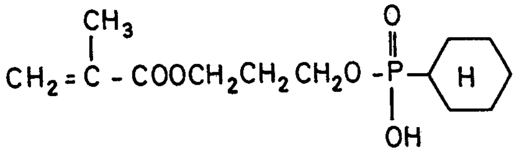


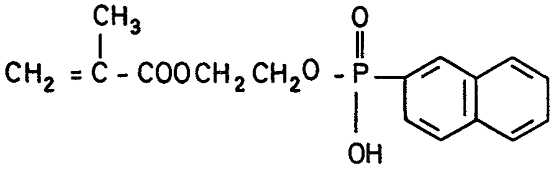


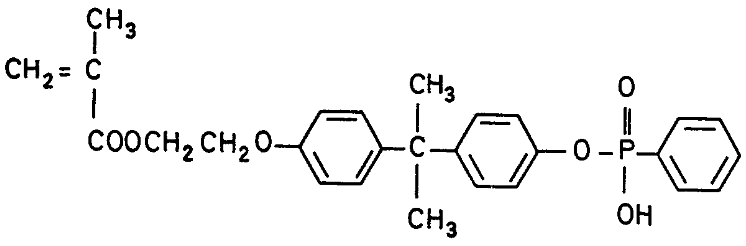


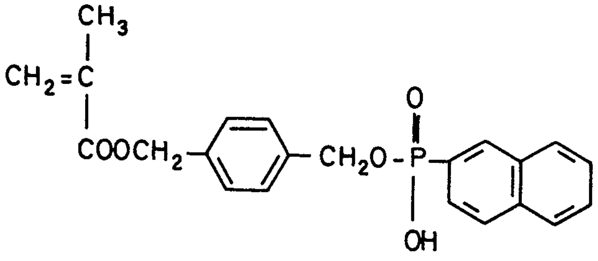


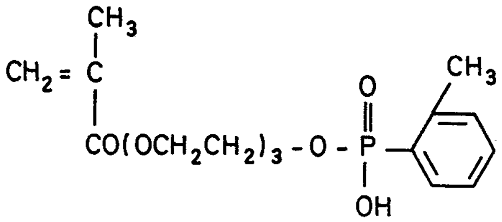


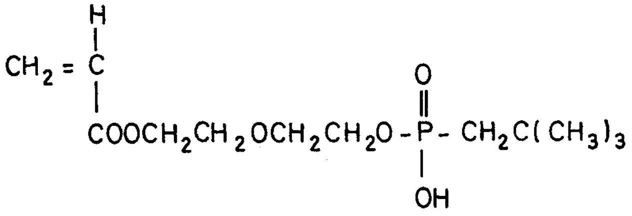




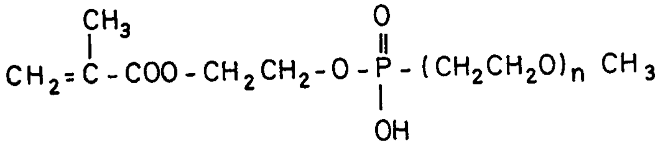




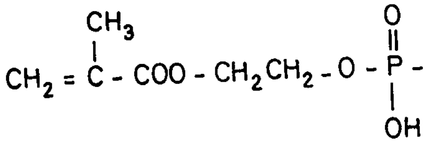




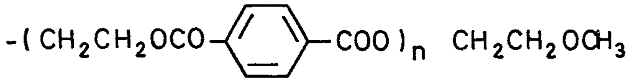
$$CH_2=\underset{\displaystyle COOCH_2CH_2OCH_2CH_2O-\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{P}}}-CH_2C(CH_3)_3}{\overset{\displaystyle H}{\overset{|}{C}}}$$

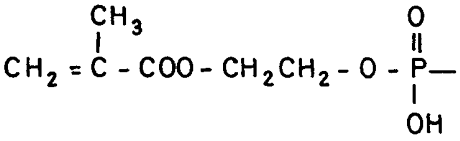


$$CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-COO-CH_2CH_2-O-\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{P}}}-(CH_2CH_2O)_n\ CH_3$$

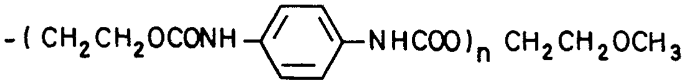


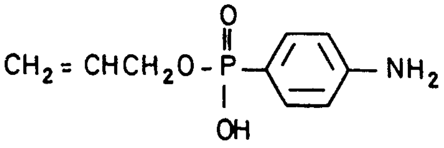
$$CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-COO-CH_2CH_2-O-\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{P}}}-$$

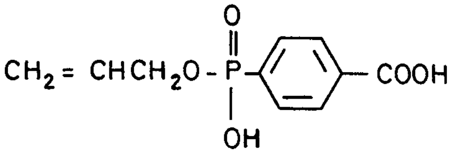


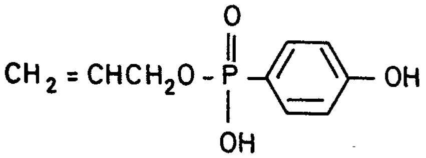


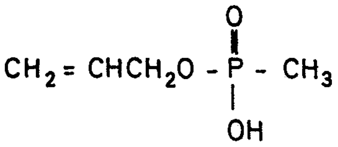
$$CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-COO-CH_2CH_2-O-\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{P}}}-$$



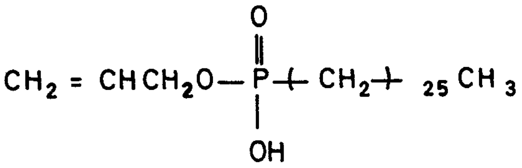




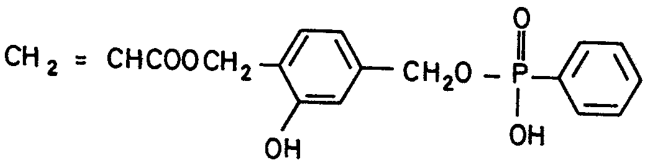


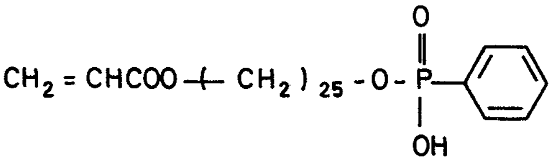


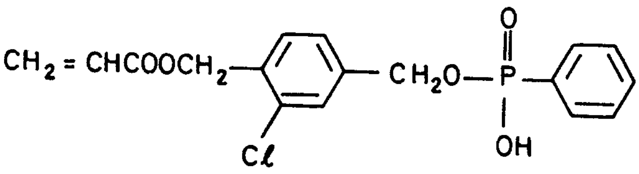
$$CH_2=CHCH_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}-CH_3$$

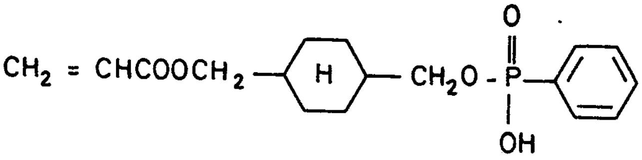


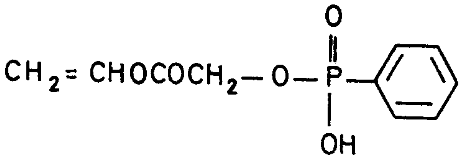
$$CH_2=CHCH_2O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}\!\left(CH_2\right)_{25}CH_3$$

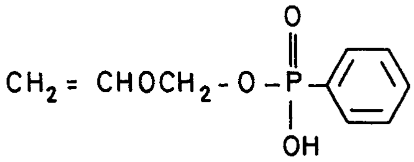


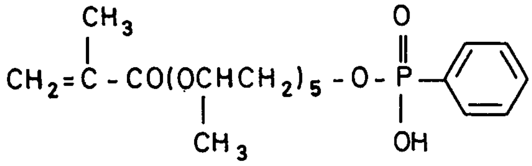


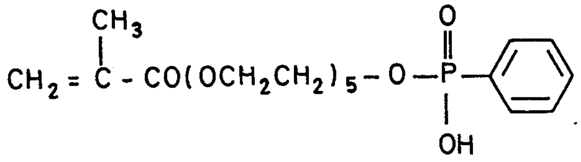


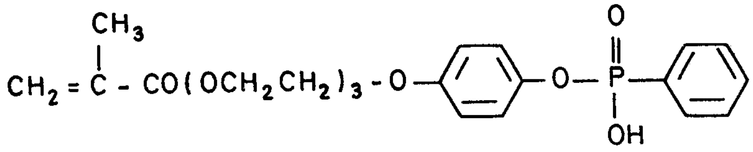


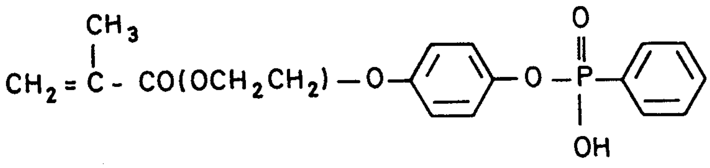


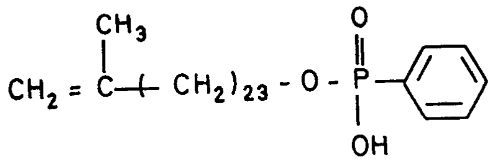




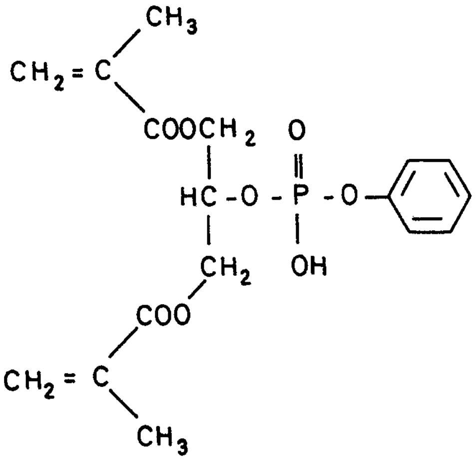


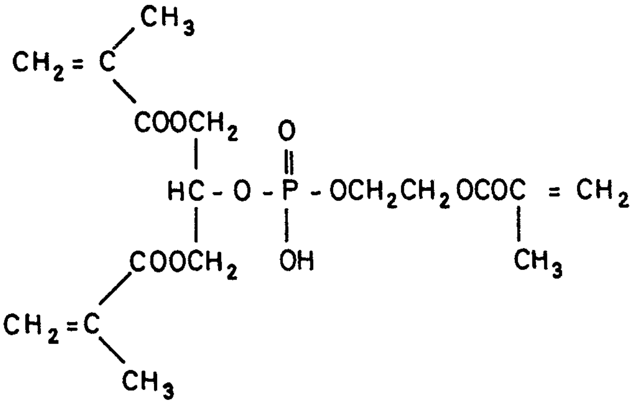


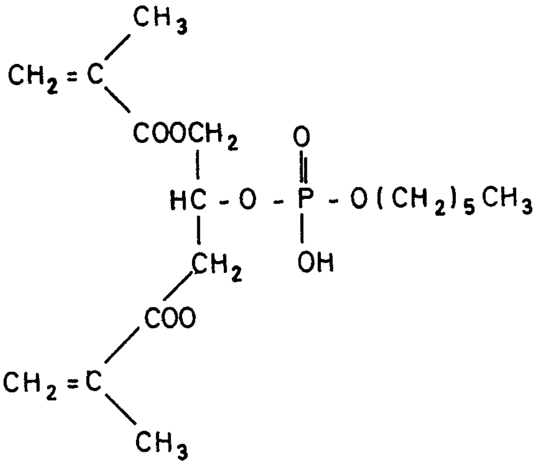


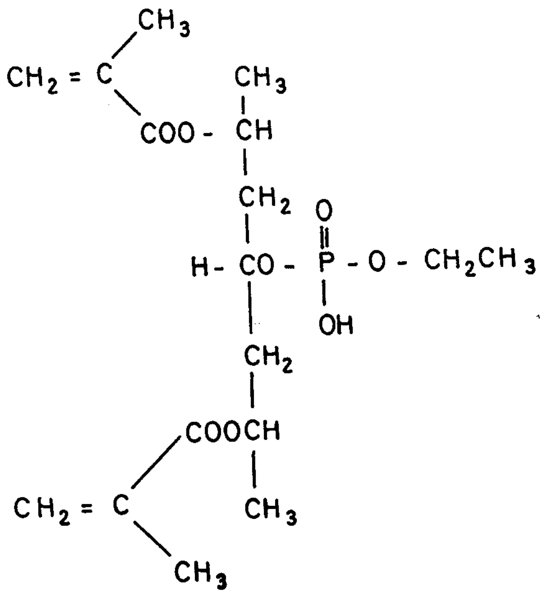


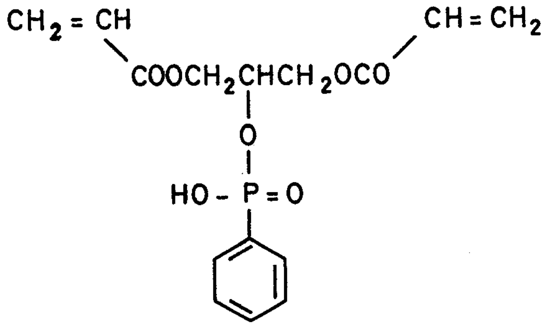
Among the compounds of formula (3):

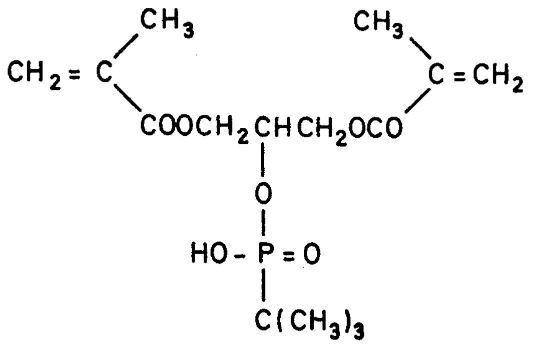




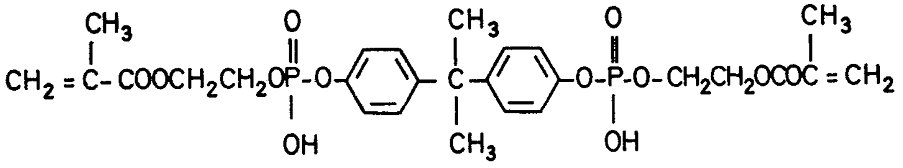


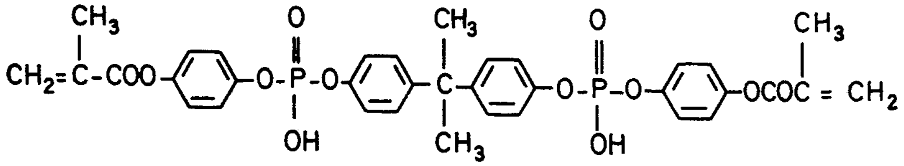


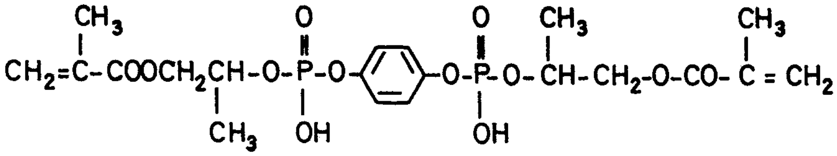


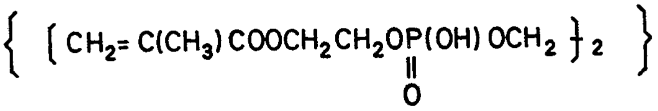


Among the compounds of formula (4), (5), or (6).

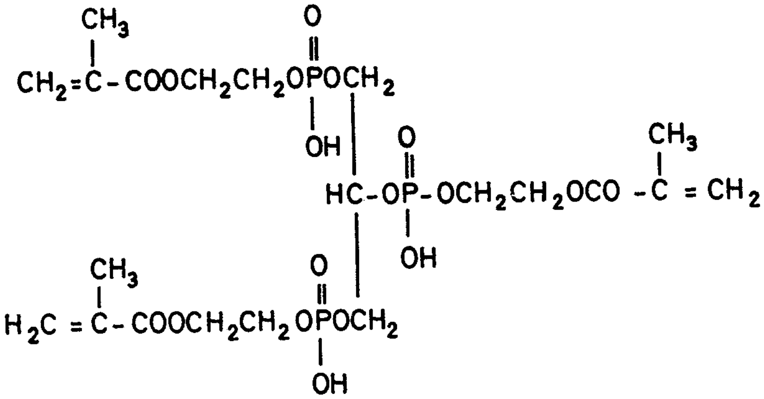


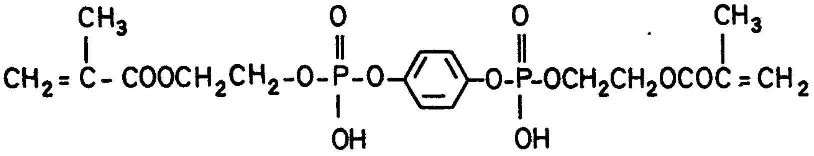


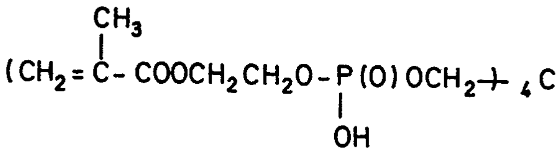




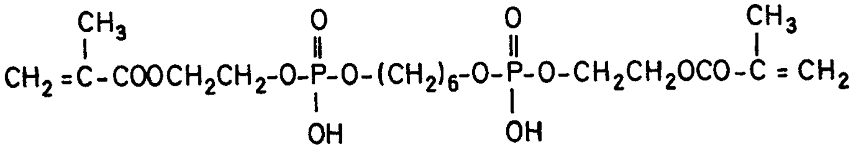
$$\{\ [CH_2{=}C(CH_3)COOCH_2CH_2O\underset{\underset{O}{\|}}{P}(OH)OCH_2\}_2\ \}$$



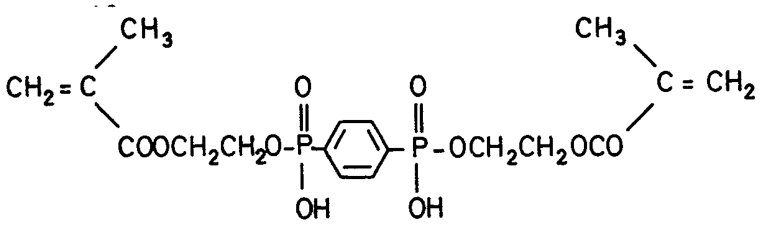


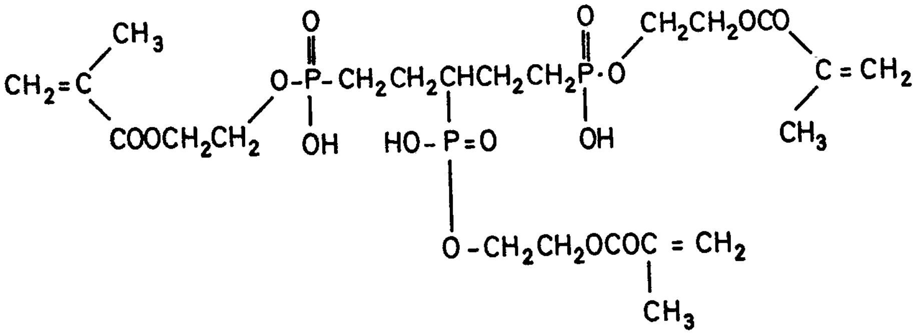


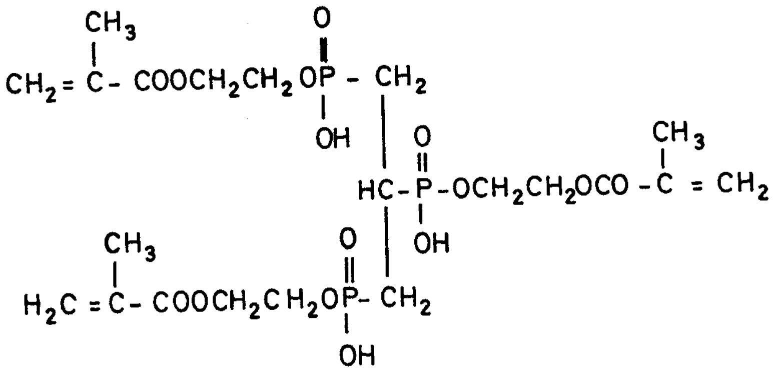
$$(CH_2{=}\overset{\overset{CH_3}{|}}{C}-COOCH_2CH_2O-\underset{\underset{OH}{|}}{P}(O)OCH_2)_4C$$



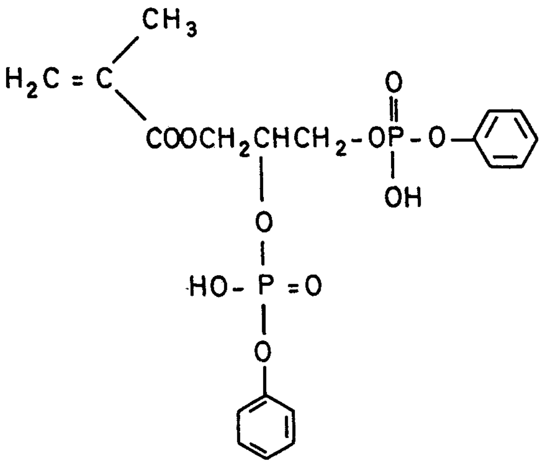
$$CH_2=C(CH_3)-COOCH_2CH_2-O-P(=O)(OH)-O-(CH_2)_6-O-P(=O)(OH)-O-CH_2CH_2OCO-C(CH_3)=CH_2$$

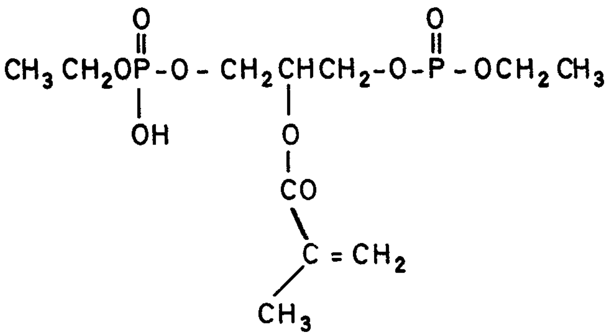


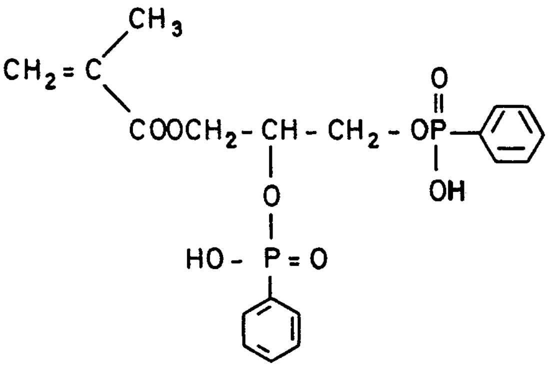


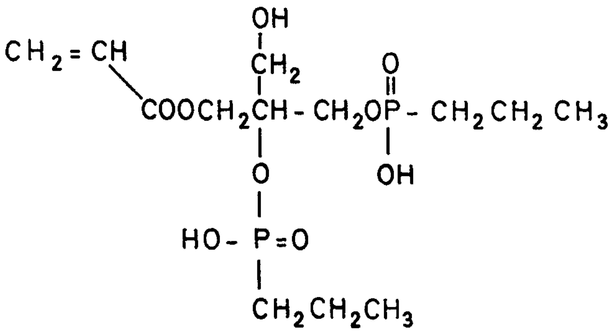


Among the compounds of formula (7):

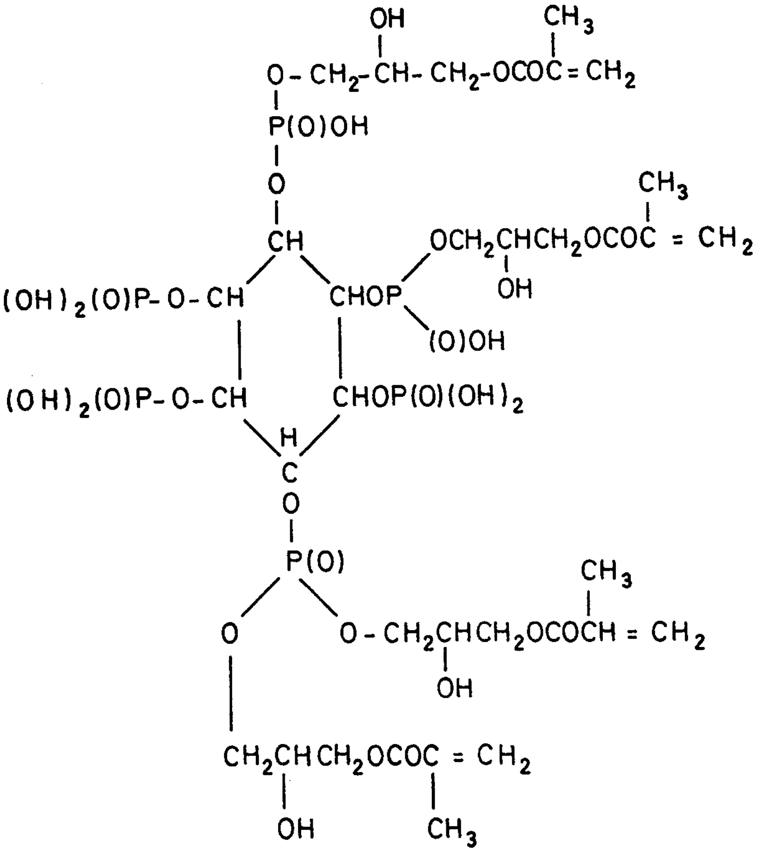




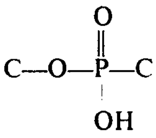




The reaction product of phytic acid and glycidyl methacrylate of the following formula is also used

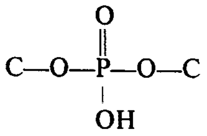


Among the foregoing compounds, the phosphonic acid ester compounds containing the



$$C—O—\overset{O}{\overset{\|}{P}}—C \atop \quad\;\; \underset{OH}{|}$$

bond are more resistant to hydrolysis, better conducive to sustained bonding strength under wet conditions and, therefore, more desirable than the phosphoric acid ester compounds containing a



$$\mathrm{C{-}O{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}{-}O{-}C}$$

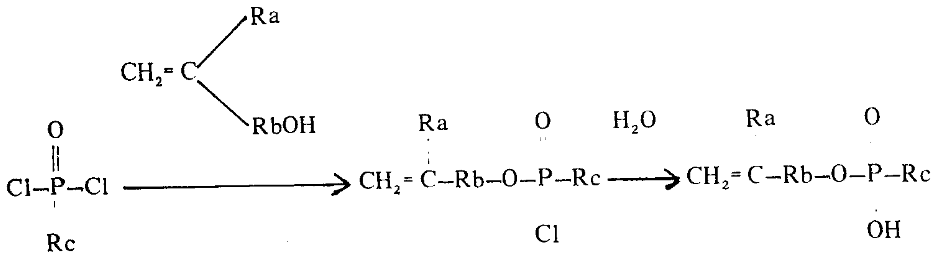
bond.

Furthermore, among the compounds of formula (2), those in which X is an alicyclic or aromatic hydrocarbon residue are superior to the compounds in which X is an aliphatic hydrocarbon residue in respect of bonding strength.

It may also be generally said that the phosphoric or phosphonic acid ester compounds containing two or more polymerizable functional groups, i.e. the compounds of formula (2), (4), (5) and (6), are more stable than the phosphoric or phosphonic acid ester, compounds containing only one polymerizable functional group, owing to the fact that even if one of the P—O—C bond is hydrolysed, the other P—O—C bond may remain intact and active.

These phosphoric or phosphonic acid ester compounds are preferably acid compounds from the standpoint of adhesive affinity for the hard tissue of the human body. However, to mitigate an irritating effect upon the tissue, the acid protons in such compounds may be partly (10 to 90 mole %) replaced in the form of salts. As the elements or compounds to form such salts may be mentioned alkali metals, e.g. sodium and potassium; alkaline earth metals, e.g. magnesium and calcium; transition elements, ammonium and amines.

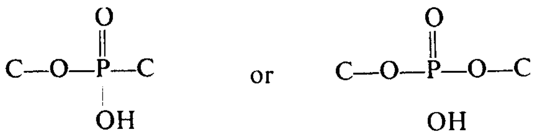
These compounds of formula (2) may normally be produced by the following reaction procedure, and the other compounds may also be produced by the similar procedure.



In the practice of this invention, the aforementioned phosphoric or phosphonic acid ester compound may be polymerized and cured at the time of application to the hard tissue of the human body or, alternatively, it may have previously been polymerized and, after admixture with another monomeric component, be cured at the time of application to the tissue. As a further alternative, it may have been previously polymerized and the resultant polymer dissolved or dispersed in a medium and applied to the hard tissue.

Among the aforementioned and other alternatives, the method comprising using the aforementioned phosphoric or phosphonic acid ester compound in monomeric form and causing it to polymerize and cure *in situ* at the time of application to the hard tissue of the human body is the most convenient to obtain the strongest adhesive bond. In such cases, while said phosphoric or phosphonic acid ester compound may be polymerized alone, it is normally copolymerized with another monomer usable in a cementing composition for the hard tissue. Therefore, the term "polymer" in the context of this invention includes copolymers with other monomers. The polymerizable monomers which may thus be used in conjunction according to this invention may be any polymerizable monomers having no injurious effects on human beings, such as methyl acrylate, ethyl acrylate, hydroxyethyl acrylate, ethylene glycol diacrylate, di-, tri- or tetraethylene glycol diacrylate, bisphenol-A diacrylate, 2,2'-bis(acryloxyethoxyphenyl) propane, 2,2'-bis(γ-acryloxy-β-hydroxypropoxyphenyl)propane. N,N-dimethylaminoethyl acrylate, glycidyl acrylate, and the all corresponding methacrylates, styrene and vinyl acetate. It is also possible to use monomers containing groups that are able to undergo low shrinkage ring-opening polymerization such as epoxy monomers, spiro-orthoesters and bicyclolactonates. There are cases in which, for the purpose of controlling the cure shrinkage, there are concomitantly used polymers such as polymethyl methacrylate, polyethyl methacrylate, polystyrene, unsaturated polyester resins and high molecular epoxy acrylate resins.

Excellent bonding affinity for the hard tissue of the human body is realized when, in the composition, the aforementioned phosphoric or phosphonic acid ester compound and/or polymer of said compound is contained in a proportion of no less than 0.1 weight percent or more, as phosphorus, of the form of



$$\mathrm{C{-}O{-}}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}\mathrm{{-}C} \quad \text{or} \quad \mathrm{C{-}O{-}}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OH}{|}}{P}}\mathrm{{-}O{-}C}$$

The curing agent may be is any agent that may effect the cure reaction at room temperature in a matter of a few minutes. For example, there may be mentioned such systems as amine-peroxide *p*-toluenesulfinic acid-peroxide, trialkylboron-peroxide and amine-salt of sulfinic acid-peroxide systems as well as ultraviolet sensitizers. In the above catalyst systems, the amine may for example be dimethyl-*p*-toluidine or N,N-diethanol-p-toluidine, and said peroxide may for example be benzoyl peroxide, while the salt of sulfinic acid may for example be sodium benzenesulfinate, sodium toluenesulfinate, sodium dodecylbenzenesulfinate or ammonium toluenesulfinate. The ultraviolet sensitizer may be benzoin methyl ether, isopropoxybenzoin, p-benzoylbenzyl bromide, benzoin phenyl ether or benzoin isobutyl ether, for instance. The use of a curing system comprising a peroxide, amine and sulfinate is particularly desirable in that it provides a higher wet bond strength than does any other curing system so far known. If necessary, there may also be incorporated a polymerization inhibitor, e.g. hydroquinone monomethyl ether or 2,6-di-tert-butyl-*p*-cresol, as well as an antioxidant, ultraviolet absorber or pigment. The adhesive cementing agent according to this invention is often used in such a manner that it is polymerized and caused to cure at the time of application to the hard tissue of the human body, and, moreover, it is expected to cure with rapidity in the neighborhood of room temperature or body temperature. Therefore, the adhesive cementing agent according to this invention must be prepared with consideration paid to the so-called pot life. As in customary with conventional cements for use on the hard tissue of the human body, there are some cases where the adhesive cementing agent of this invention is supplied to doctors or dentists in at least two separate packages, one of which contains the aforementioned phosphoric or phosphonic acid ester compound.

In such cases, the clinician admixes the contents of a package with the contents of the other package or packages to produce a cured compound. In other cases the clinician irradiates the contents of a single package with ultraviolet or other rays to obtain a cured compound.

The adhesive cementing agent according to this invention, when used as compounded with a filling agent, may improve the bonding affinity of the cement for the hard tissue of the human body. Alternatively, the adhesive cementing agent may be coated onto the exposed surface of the tooth or bone and then the known cement or restorative applied, in which case the adhesion of the cement or restorative to the hard tissue is improved. The adhesive cementing agent of this invention may also be used as a adhesive agent for inlays and crowns, because of the good affinity to metal. Therefore, the term "adhesive cementing agents" in the context of this invention includes, *inter alia* dental adhesive agents for bonding the dental filling material, inlays or crowns to the tooth, dental filler, dental restorative, dental cement, bone cement for fixation of artificial joints and adhesive agents for the treatment of a complex fracture of bone. The following description concerns the preferred use for the present adhesive cementing agent, i.e. as a cement for a dental filling composition or between the tooth and the filler. In such applications, the use of the phosphoric or phosphonic acid ester compound or polymer thereof in admixture with a known cement results in a significantly improved bond with the hard tissue of the human body without resort to any modification in conventional procedure.

When the adhesive cementing agent of this invention is used as a filling composition, the composition desirably comprises the aforementioned phosphoric or phosphonic acid ester compound, a polymerizable monomer, a filler material and a curing agent. Such composition is polymerized after filling into the cavity of the tooth and said phosphoric or phosphonic acid ester compound, on polymerization, displays an intimate bonding effect, providing a strong adhesion between the tooth and the filling composition without use of any external adhesive agent. The composition preferably contains 2 to 50 weight percent, particularly 3 to 10 weight percent, of the phosphoric or phosphonic acid ester compound relative to the polymerizable monomer. No adequate bonding effect is achieved when the proportion is less, whereas a larger amount of the phosphoric or phosphonic acid ester compound tends to cause a depression in hardness. The polymerizable monomers usable together with the aforementioned phosphoric or phosphonic acid ester compound are the monomers normally used for example, bisphenol A diglycidyl methacrylate as mentioned in U.S. Patent No. 3,066,122, bisphenol-A dimethacrylate, 2,2-bis(4-methacryloxyethoxyphenyl) propane, 2,2-bis(4-methacryloxypropoxyphenyl) propane, xylylene glycol dimethacrylate, polyfunctional methacrylate esters (e.g. neopentyl glycol dimethacrylate, ethylene glycol dimethacrylate, triethylene glycol dimethacrylate and trimethylolpropane trimethacrylate). Normally these monomers are incorporated in a proportion of 10 to 50 weight percent based on the weight of the composition. The filler and curing agent may each be of the conventional variety. As the filler, silica powder, aluminum oxide powder and quartz powder silanated and having a particle diameter of 10 to 50 μ are particularly desirable.

Where the adhesive agent according to this invention is used as a cementing composition for bonding the dental filling material to the tooth, it is applied by priming between the tooth and filling composition. This application may be accomplished by any of the following techniques.

Thus, one of the following composition is applied to the interface between the tooth and the dental filling composition, inlay or the like.

(1) A composition comprising a solution, in an organic solvent having a boiling point not exceeding 80°C, of the aforementioned phosphoric or phosphonic acid

ester compound, the amount of which is not less than 5 weight %, preferably 5 to 20 weight %, based on the solution;

(2) A composition comprising a polymerizable monomer incorporating, the aforementioned phosphoric or phosphonic acid ester compound, the amount of which is not less than 2 weight % and preferably 5 to 20 weight %, relative to the said polymerizable monomer; or

(3) A composition comprising a polymerizable monomer, a curing agent, if necessary, a powdery vinyl polymer, and, incorporated in the said monomer, the aforementioned phosphoric or phosphonic acid ester compound, the amount of which is not less than 2 weight % and preferably 3 to 15 weight %, based on said monomer, the proportion of said monomer being 30 to 99 weight percent of the composition.

The desired bonding effect is not attained when the ester compound is less than the aforementioned range in each instance, while an excess of the compound tends to detract from the water resistance of the composition.

The organic solvent in composition (1) is a low-boiling solvent substantially non-irritating to the dental pulp, such as ethanol, ethyl ether or chloroform. The polymerizable monomer in composition (2) is desirably based on a hydrophilic acrylic acid ester or methacrylic acid ester that has an affinity for the wet tooth. Preferred examples of such esters include hydroxyalkyl methacrylates such as 2-hydroxyethyl methacrylate and 3-hydroxypropyl methacrylate. As a component of composition (3), methyl methacrylate may be used. Further, for the purposes of improving the hardness and water-absorption characteristics, use is made of an aromatic methacrylate ester such as bisphenol-A diglycidyl methacrylate and bisphenol A dimethacrylate, as well as the forementioned polyfunctional methacrylate esters.

It will be apparent that by use of the adhesive cementing agent according to this invention an intimate bond that has never been achieved by the prior art is obtained. It has further been established that this bond strength remains unaffected over a long time even under wet conditions, e.g. in the mouth or body. Furthermore, because clinically the present invention may be used by the conventional techniques without any substantial modification to obtain an intimate bond with the hard tissues of the human body, clinicians may use the adhesive cementing agent of this invention with facility. It should also be in order to mention that, within the best knowledge of the present inventors, the phosphoric or phosphonic acid ester compound according to this invention has only negligible oral toxicity and no extraordinary injurious effects upon the pulp tissue.

The following Examples are further illustrative but by no means limitative of this invention. All parts and percentages in the Examples are by weight unless otherwise stated; the words 'Instron', 'Adaptic' and 'Autograph' are trade marks.

Example 1.

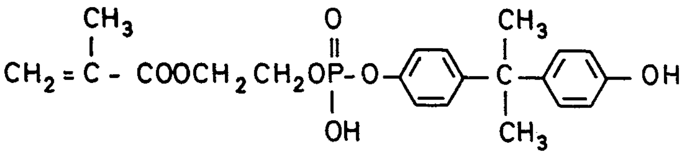
The resin compositions indicated below were tested for bond strength with the wet dentin and enamel.

The crown of a fresh bovine tooth or a bar of fresh ivory was ground flat and finished with an emery paper No. 6/0 until the enamel or dentin was exposed. This bovine tooth or ivory bar was immersed in water for more than a day and, immediately before testing, the surface was wiped free of moisture. As to the bovine tooth, the enamel was etched with 50% phosphoric acid, washed with water and wiped free of moisture. The bovine tooth and ivory bar were coated with one of the test resin compositions. An acrylic resin bar was superimposed on the resin coat and the latter was allowed to cure. Thereafter, the assembly was held in water at 37°C for 72 hours. The samples were then pulled apart to determine the bond strength. The average bond strength for 8 specimens is shown in Table 1.

A: A resin composition comprising a mixture of 50 parts of polymethyl methacrylate (mol. wt. 130,000), 40 parts of methyl methacrylate, 10 parts of ethylene glycol dimethacrylate, 2 parts of benzoyl peroxide, 4 parts of sodium *p*-toluenesulfinate and 2 weight parts of dimethyl-*p*-toluidine.

B ~ N: A mixture of 100 parts of Resin Composition A and 10 parts of one of the following phosphoric or phosphonic acid ester compounds.

B:



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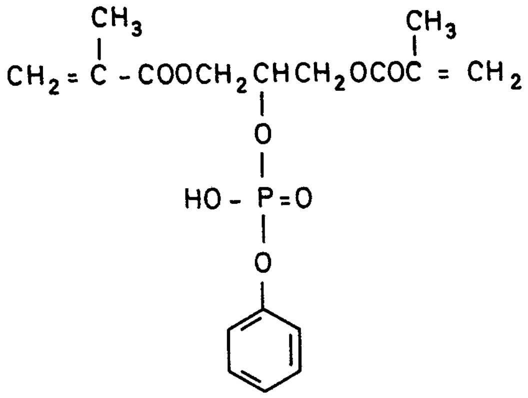
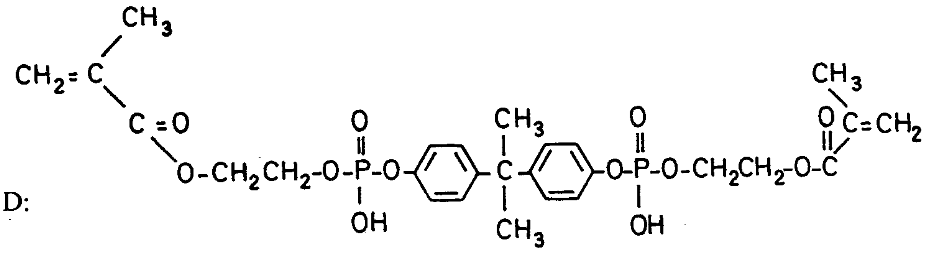


D:



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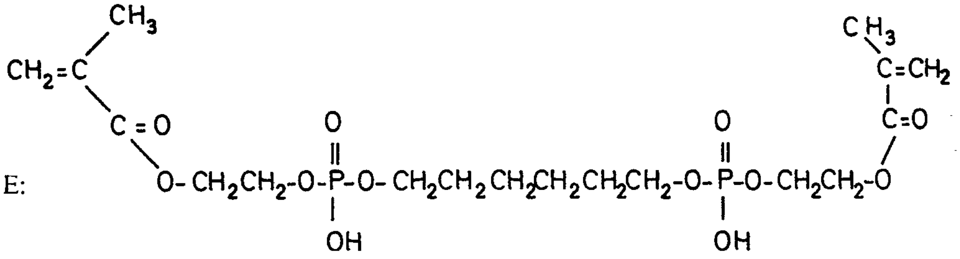

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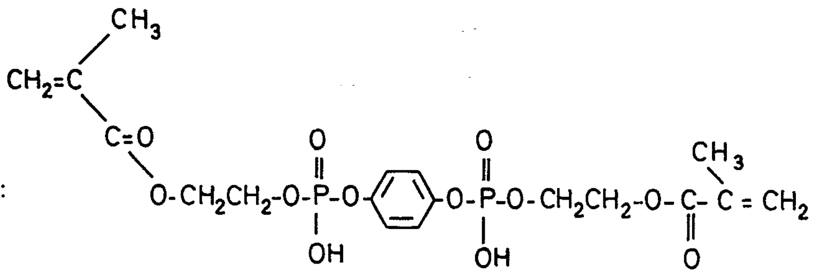
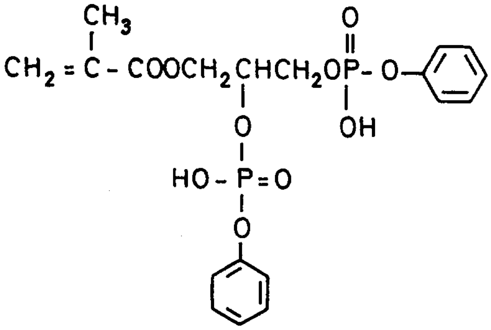


G:



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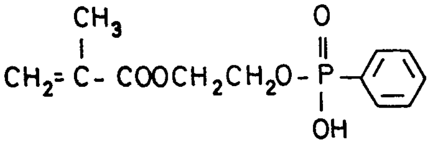

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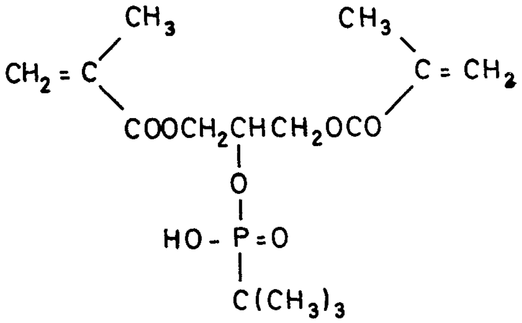
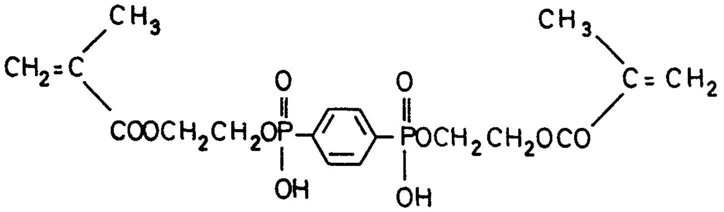
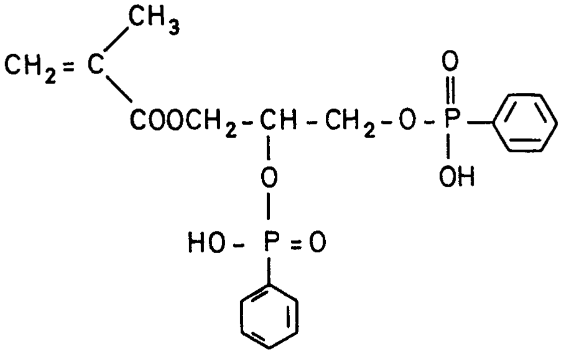


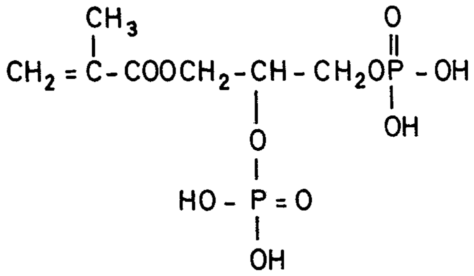
J:



K:

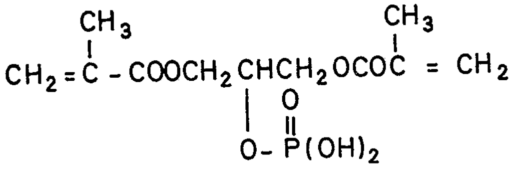


L: (control)



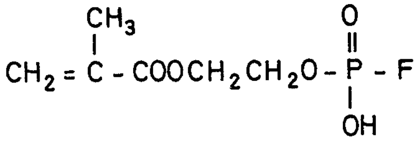
$$CH_2=\overset{\overset{\textstyle CH_3}{|}}{C}-COOCH_2-\underset{\underset{\underset{\underset{\textstyle HO-\underset{\underset{\textstyle OH}{|}}{P}=O}{|}}{O}}{|}}{CH}-CH_2O\underset{\underset{\textstyle OH}{|}}{\overset{\overset{\textstyle O}{\|}}{P}}-OH$$

M: (control)



$$CH_2=\overset{\overset{\textstyle CH_3}{|}}{C}-COOCH_2\underset{\underset{\textstyle O-\overset{\overset{\textstyle O}{\|}}{P}(OH)_2}{|}}{CH}CH_2OCO\overset{\overset{\textstyle CH_3}{|}}{C}=CH_2$$

N: (control)



$$CH_2=\overset{\overset{\textstyle CH_3}{|}}{C}-COOCH_2CH_2O-\underset{\underset{\textstyle OH}{|}}{\overset{\overset{\textstyle O}{\|}}{P}}-F$$

TABLE 1

Resin Composition	Bond Strength (kg/cm²)	
	With dentin	With enamel
A	32	63
B	121	107
C	160	109
D	151	–
E	138	–
F	146	–
G	154	96
H	170	115
I	90	112
J	163	110
K	187	89
L	21	114
M	25	92
N	79	104

It will be apparent from Table 1 that the adhesive cementing agents containing a phosphoric or phosphonic acid ester compound according to this invention (B—K) are superior to the adhesive cementing agent (A) free of the phosphoric or phosphonic acid ester compound in bonding affinity to both dentin and enamel. Moreover, while the cements of the present invention give no significant difference in bond strengh with respect to tooth enamel, as compared with the phosphoric acid compounds (L—N) that are different from the phosphoric or phosphonic acid esters according to this invention in chemical structure, they are by far superior in bond strength with respect to dentin.

Example 2.

The following powder-liquid cementing systems containing the phosphoric acid ester compounds were prepared and, using ivory bars in Example 1, these systems were tested for bonding affinities.

System A:

Two parts of benzoyl peroxide was added to 98 parts of polymethyl methacrylate powder, followed by thorough mixing to prepare a powdery component. To 95 parts of methyl methacrylate was added 5 parts of 2-methacryloxyethyl-phenyl acid phosphate (*1 below) together with 2.5 parts of *p*-toluenesulfinic acid to prepare a liquid component.

System B:

To 98 parts of polymethyl methacrylate powder was added 2 parts of benzoyl peroxide, followed by thorough mixing to prepare a powdery component. To 95 parts of methyl methacrylate was added 5 parts of 2-methacryloxyethyl 2-bromoethyl acid phosphate (*2 below) together with 2.5 weight parts of ptoluenesulfinic acid to prepare a liquid component.

The bond stengths found were 162 kg/cm^2 for System A and 90 kg/cm^2 for System B.

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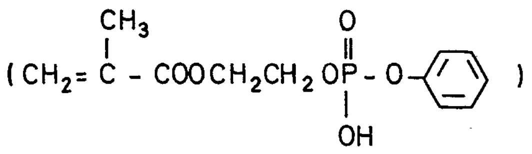

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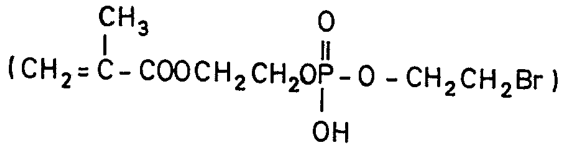

$$(CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-COOCH_2CH_2O\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}}-O-CH_2CH_2Br)$$

Example 3.

Coating compositions C and D were prepared by diluting the phosphoric acid ester monomer with a polymerizable monomer.

Composition C: This composition was prepared by diluting 10 parts of 2-methacryloxyethyl phenyl acid phosphate with 90 parts of 2-hydroxyethyl methacrylate.

Composition D: This composition was prepared by diluting 10 parts of 2-methacryloxyethyl 2-bromoethyl acid phosphate with 90 parts of 2-hydroxyoxyethyl methacrylate.

Separately, the following two kinds of filling pastes were prepared from a polymerizable monomer, an inorganic filler and a curing agent.

P_1 Paste:

Bisphenol-A diglycidyl methacrylate (hereinafter referred to as Bis-GMA)	16.8 parts
Triethylene glycol dimethyacrylate	2.8 parts
Silanated quartz powder	80.1 parts
N,N-diethanol-p-toluidine	0.3 parts

P_2 Paste:

Bis-GMA	16.8 parts
Triethylene glycol dimethacrylate	2.8 parts
Silanated quartz powder	80.0 parts
Benzoyl peroxide	0.4 parts

By means of a small brush, either Composition C or Composition D was sparingly applied to the end surface of an ivory bar. Then, the above two filling pastes were kneaded together for 30 seconds and applied in superimposition on the coated primer. A bar of acrylic resin was then placed in abutment against the ivory bar end-to-end and the system was allowed to cure *in situ* to provide a bond between the bars. The bond strength was determined by the same procedure as hereinbefore described. The bond strength values were as high as 120 kg/cm^2 when Composition C was used as a primer coating, and 110 kg/cm^2 when Composition D was so used. In a control run, where neither Composition C nor Composition D was used, no bond was established between the filling agent and dentin.

An extracted human molar was processed with an air turbine to produce a cavity about 4 mm in dia. and 3.5 mm deep in the neck portion of the tooth and the enamel of the tooth was etched with 50% aqueous phosphoric acid and rinsed well with water. Then the cavity was dried with a current of air. After a thin coat of Composition C or Composition D had been applied to the wall of the cavity, the above mixed filling paste was filled into the same cavity. The cure time was 4 minutes. The tooth was dipped in solutions of fuchsin at 0°C and 60°C, in turn and 60 times each for a period of 1 minute per dipping. The marginal sealing effect was investigated in terms of dye penetration. The test showed no evidence of dye penetration.

Example 4.

14.5 parts of Bis-GMA, 3.0 parts of neopentyl glycol dimethacrylate, 1.8 parts of 2-methacryloxyethyl phenyl acid phosphate, 80.7 parts of the same silanated quartz powder as that used in Example 3 and 0.5 parts of benzoyl peroxide were kneaded into a paste and, immediately before use, *p*-toluenesulfinic acid was added in a proportion of 1.0 part based on the total weight. This filling composition cured in about 5 minutes.

By the same procedure as Example 3, the above filling composition was filled into an extracted molar and examined for a marginal sealing effect around the cavity. No ingress of the dye was observed, attesting to the excellent sealing effect of the composition. In contrast, with a filling composition free from the phosphoric acid ester compound as used under the same conditions as above, the penetration of dye in many instances reached the bottom of the cavity, providing only poor sealing effects.

Example 5.

The following components E and F were prepared as a cold-cure powder-liquid resin system.

Component E:

95 parts of polymethyl methacrylate (mol. wt. 250,000) was mixed with 3 parts of sodium *p*-toluenesulfinate and 2 parts of dibenzoyl peroxide to prepare a powdery component.

Component F:

80 parts of methyl methacrylate was mixed with 10 parts of ethylene glycol dimethacrylate, 9 parts of bis-(2-methacryloxyethyl) acid phosphate (*1) and 1 part of N,N′-diethanol-*p*-toluidine to prepare a liquid component.

Equal weights of components E and F were taken in a glass vessel and stirred together for 1 minute. The resultant mixture was coated onto the end face of a bar of ivory and of an acrylic resin bar and the two end faces were abutted against each other. The bond strength achieved between the bars as determined by the procedure described bereinbefore is shown in Table 2. A stable high bond strength was evident even after prolonged immersion in water.

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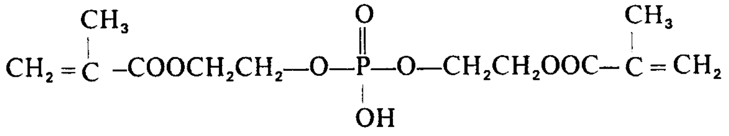


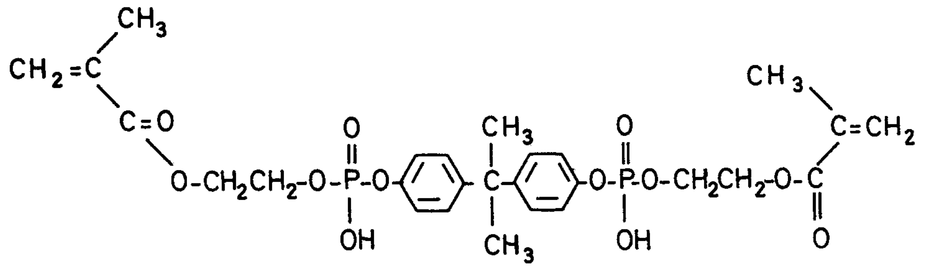
$$CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-COOCH_2CH_2-O-\underset{\displaystyle OH}{\underset{|}{\overset{\displaystyle O}{\overset{\|}{P}}}}-O-CH_2CH_2OOC-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2$$

TABLE 2

No. of days of immersion in water at 37°C	1 day	7 days	30 days	90 days
Average bond strength (kg/cm^2)	150 ± 45	173 ± 47	138 ± 50	165 ± 65

Example 6.

40 parts of diethylene glycol dimethacrylate was mixed well with 60 parts of bisphenol-A diglycidyl methacrylate and 330 parts of silanated α-quartz powder (particle diam. $10 \sim 50\ \mu$) and the mixture was divided into two equal parts. To one of the halves was added 10 parts of the compound of formula:



together with 2 parts of benzoyl peroxide. To the other half was added 2 parts of N,N-dimethyl-*p*-toluidine together with 2 parts of sodium *p*-toluenesulfinate. Before use, equal portions of the two pastes were thoroughly kneaded together, applied between bars of ivory and allowed to cure *in situ*. The mixed paste started curing about 3 minutes after the start of admixing and set sufficiently in about 10 minutes. The joined bar of ivory was maintained in water at 37°C for 3 days, after which the bond strength was determined on an Instron tensile tester. While there was some variation between specimens, the range of bond strengths for ten bars was 108 to 190 kg/cm^2, the average being 178 kg/cm^2.

Portions of the above two pastes were admixed and filled into a #1 cavity formed in an extracted tooth, after phosphoric acid etching. Such specimens were subjected to a percolation test which comprised dipping them in aqueous dye baths at 4° and 60°C, in turn and for a total of 100 times each, one minute per dipping. Substantially none of the specimens tested betrayed a penetration of the dye into the dentin, thus attesting to the satisfactory and improved bond between the tooth and filling agent.

Example 7.

20 parts of the same phosphoric acid ester compound as used in Example 6 was mixed with a viscous fluid consisting of 30 parts of tetraethylene glycol dimethacrylate, 10 parts of hydroxyethyl methacrylate, 60 parts of methyl methacrylate and 20 parts of polymethyl methacrylate (mol. wt. 130,000). The resultant liquid composition was used to coat the etched (phosphoric acid) walls of cavities in extracted teeth, which cavities has been formed by the removal of the decayed portion of the dentin, and had no retention form. Then, a commercial composite resin (Johnson & Johnson: Adaptic) was filled into the cavities. These tooth specimens were subjected to a percolation test similar to that described in Example 6. The results indicated quite satisfactory marginal sealing effects.

Example 8.

10 parts of the same phosphoric acid ester compound as that used in Example 6 was incorporated in a viscous fluid consisting of 10 parts of tetraethylene glycol dimethacrylate, 90 parts of methyl methacrylate and 20 parts of polymethyl methacrylate (mol. wt. 130,000).

To this fluid was added 1 % of benzoyl peroxide together with 1 % of dimethyl-*p*-toluidine and 3 % of sodium *p*-toluenesulfinate. The mixture was coated onto the surface of a tooth and a polycarbonate orthodontial bracket was fitted over the coated tooth. The bond between the tooth and bracket was quite satisfactory and remained stable over a long time.

Example 9.

As powder-liquid cementing systems, compositions G and H were prepared using different phosphonic acid monomers.

System G.

To 100 parts of polymethyl methacrylate powder was added 2 weight parts of benzoyl peroxide together with 3 parts of sodium *p*-toluenesulfinate and the mixture was stirred well to prepare a powdery component. To a mixture of 80 parts of methyl methacrylate and 10 parts of ethylene glycol dimethacrylate was added 10 parts of 2-methacryloxyethyl phenyl phosphonic acid (*1) together with 1.0 parts of N,N′-diethanol-*p*-toluidine to prepare a liquid component.

System H:

To 100 parts of polymethyl methacrylate powder was added 2 parts of benzoyl peroxide together with 3 parts of sodium *p*-toluenesulfinate and the mixture was blended well to prepare a powdery component. To a mixture of 80 parts of methyl methacrylate and 10 parts of ethylene glycol dimethacrylate was added 10 parts of 2-methacryloxyethyl isobutyl-phosphonic acid (*2) together with 1.0 part of N,N′-diethanol-p-toluidine to prepare a liquid component. Equal weights of the powder and fluid of the above system G or H were kneaded together and the mixture was used to coat the end face of a rectangular bar of ivory to provide a relatively thick coat. A rectangular acrylic resin bar with a cross sectional area of 10 × 10 mm was butted against the above coated face and the system was allowed to cure *in situ*.

The joined bar was immersed in water at 37°C for 48 hours, after which the bond strength was determined using an autograph.

In the case of System G, the average bond strength was 160 kg/cm², while System H provided an average bond strength of 140 kg/cm². These values are considerably higher than the average value of 35 kg/cm² for the corresponding systems G and H free of the phosphonic acid ester compound.

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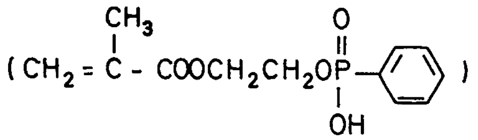

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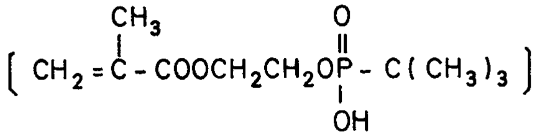


$$\left[\, CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-COOCH_2CH_2O\overset{\displaystyle O}{\overset{\|}{\underset{\displaystyle OH}{\underset{|}{P}}}}-C(CH_3)_3 \,\right]$$

Example 10.

The following system containing the phosphonic acid ester compound of this invention was prepared.

Component I:

Bisphenol-A diglycidyl dimethacrylate	14.3 parts
2-Methacryloxyethyl phenyl phosphonic acid	4.4 parts
Triethylene glycol dimethacrylate	3.3 parts
Silanated α-quartz powder	77.5 parts
Benzoyl peroxide	0.45 part
Hydroquinone monomethyl ether	0.05 part

Component J:

Bisphenol-A diglycidyl dimethacrylate	10.7 parts
Triethylene glycol dimethacrylate	3.3 parts
Silanated α-quartz powder	77.2 parts
Sodium p-toluenesulfinate	0.55 part

N,N′-diethanol-p-toluidine	·0.2 part
Hydroquinone monomethyl ether	0.05 part

Equal weights of Component I and Component J were taken and thoroughly kneaded together. The resultant system cured in 3 minutes.

The bond strength provided by the kneaded paste with respect to a bar of ivory was determined. The bond.strength after 24 hours' immersion in water was 35 kg/cm². An extracted healthy human front tooth was processed with an air turbine in the routine manner to form a cavity 3 mm in diameter and 2 mm deep and, then, the enamel was etched with 50% aqueous phosphoric acid, rinsed with water and dried with a current of air. The equal weight portions of component I and component J were kneaded and the obtained paste was filled into the cavity. The tooth specimen was dipped in aqueous solutions of fuchsin at 0°C and 60°C, in turn and for a total of 60 times, one minute per dipping. This percolation test showed substantially no evidence of dye penetration.

Example 11.

10 parts of 2-methacryloxyethyl phenyl phosphonic acid was mixed with a fluid consisting of 30 parts of tetraethylene glycol dimethacrylate, 40 parts of 2-hydroxyethyl methacrylate and 20 parts of methyl methacrylate.

To this fluid was added 3 % of sodium p-toluenesulfinate and, after thorough mixing, the mixture was applied to the end faces of wet bars of ivory with a small brush to provide a thin coat. Then, equal parts of the two pastes of the commercial Adaptic (trade name, Johnson & Johnson) were mixed well and inserted and allowed to cure between the bars of ivory. The above procedure provided an intimate bond. The joined bar was maintained in water at 37°C for 1 to 30 days and the bond strength values were determined.

The results are set forth in Table 3.

TABLE 3

No. of days of immersion in water	1	14	30
Bond strength (kg/cm²)	155	142	151

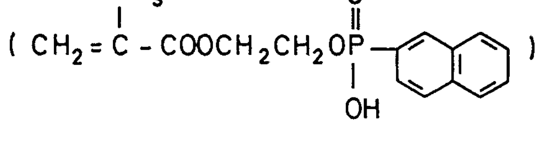
Using an extracted healthy human front tooth, the above composition was used to coat the cavity in the same manner as above and the tooth was subjected to a percolation test similar to that described in Example 6. The result was an excellent marginal seal.

Example 12.

The surface of an extracted healthy tooth was treated with a 50% aqueous solution of phosphoric acid and rinsed well with water. 10 parts of (2-methacryloxyethyl)-β-naphthylphosphonic acid (*1) was mixed with 10 parts of tetraethylene glycol dimethacrylate, 80 parts of methyl methacrylate and 30 parts of polymethyl methacrylate (mol. wt. 130,000).

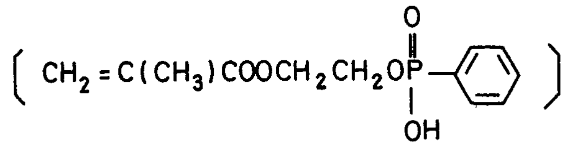
To this fluid was added 1% of benzoyl peroxide together with 1 % of dimethyl-p-toluidine and 3% of sodium p-toluenesulfinate and, after thorough mixing, the mixture was coated onto the surface of the above tooth. Then, a polycarbonate orthodontial bracket was fitted over the coated tooth. There was obtained an excellent bond between the tooth and bracket, the bond strength being stable over a long period.

*1



Example 13.

A three-necked flask of 300 ml capacity, fitted with a stirrer, condenser and thermometer, was charged with 200 g of toluene, 40 g of methyl methacrylate, 2 g of (2-methacryloxyethyl) phenylphosphonic acid (*1) and 0.2 g of benzoyl peroxide.

*1

$\left(CH_2=C(CH_3)COOCH_2CH_2O\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-C_6H_5 \right)$

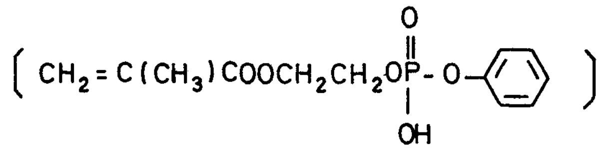
Under vigorous stirring, the polymerization reaction was continued at 90°C for 3 hours. After cooling, the reaction mixture was added to a large quantity of ethyl ether to reprecipitate the polymer. The polymer was dried well and comminuted to prepare a microfine powder not larger than 200 mesh.

To 100 parts of this finely divided polymer was added 3 parts of sodium p-toluenesulfinate together with 2 parts of benzoyl peroxide, followed by thorough mixing to prepare a powdery component.

To a mixture of 80 parts of methyl methacrylate and 20 parts of ethylene glycol dimethacrylate was added 1 part of N,N'-diethanol-*p*-toluidine. The resultant monomeric composition and the above powdery component were used to coat the end face of a rectangular bar of ivory with a brush to provide a comparatively thick coat and the end face of a rectangular bar of acrylic resin was placed in abuttment against the above coated end face.

The joined bar was immersed in water at 37°C for 24 hours, and, then, the bond strength was determined using an Autograph. The average bond strength for 10 specimens was as high as 154 kg/cm².

A composition was prepared by the same procedure as above except that (2-methacryloxyethyl) phenyl phosphoric acid


$\left(CH_2=C(CH_3)COOCH_2CH_2O\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-O-C_6H_5 \right)$

was used in lieu of the (2-methacryloxyethyl)phosphoric acid and the bond strength was determined under the same conditions as above. The average bond strength was 162 kg/cm².

Example 14.

The following components were prepared for a two-liquid cementing system for liner use and a two-paste composite resin system.

Component K (liquid)

2-Methacryloxyethyl phenyl acid phosphate	20 parts
Bisphenol-A diglycidyl methacrylate	10 parts
Neopentyl glycol dimethacrylate	60 parts
Methacrylic acid	10 parts
Benzoyl peroxide	3 parts
Hydroquinone monomethyl ether	0.05 part

Component L (Liquid)

2 Hydroxyethyl methacrylate	40 parts
Bisphenol-A diglycidyl methacrylate	40 parts
Diethylene glycol dimethacrylate	20 parts
Sodium benzene sulfinate	2 parts
N,N-diethanol-p-toluidine	3 parts
Hydroquinone monomethyl ether	0.05 part

Component M

The same paste as P_1 used in Example 3.

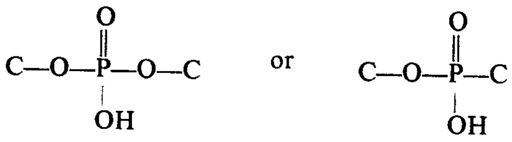
Component N

The same paste as P_2 used in Example 3.

In an extracted tooth a cavity about 2 mm in dia. and 4 mm deep was formed. The cavity and the enamel part around the cavity were coated with the paste comprising 50% phosphoric acid aqueous solution and 10% Aerosil to the said solution, then rinsed with water after 1 minute and dried with a current of air. Then equal weights of component K and component L were mixed to coat on the wall of the cavity and the enamel part around the cavity. Then equal weights of component M and component N were kneaded together and filled into the cavity. After the lapse of 5 minutes, the filled cavity was polished with a diamond tool and then with a paste-like finishing agent. The tooth was, from the aesthetical and mechanical view point, perfectly repaired with this treatment. A quite satisfactory marginal sealing effect was observed.

WHAT WE CLAIM IS:—

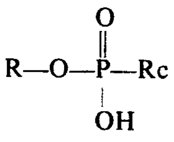
1. An adhesive cementing agent for the hard tissues of the human body comprising (a) a phosphoric and/or phosphonic acid ester compound containing at least one radical-polymerizable vinyl group and at least one



$$\mathrm{C{-}O{-}}\underset{\underset{\displaystyle \mathrm{OH}}{|}}{\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{P}}}\mathrm{{-}O{-}C} \quad \text{or} \quad \mathrm{C{-}O{-}}\underset{\underset{\displaystyle \mathrm{OH}}{|}}{\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{P}}}\mathrm{{-}C}$$

bond, or a high-molecular-weight compound obtainable by polymerizing said compound either alone or as a comonomeric unit, (b) a radical-copolymerizable comonomer, and (c) a curing agent, in which the weight of phosphorus of component (a) is not less than 0.1% of the weight of the adhesive cementing agent in actual use.

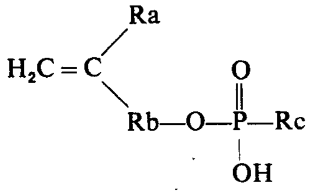
2. An adhesive cementing agent as claimed in claim 1 in which the phosphoric or phosphonic acid ester compound is a compound of the general formula:



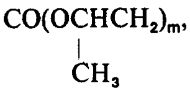
$$\mathrm{R{-}O{-}}\underset{\underset{\displaystyle \mathrm{OH}}{|}}{\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{P}}}\mathrm{{-}Rc}$$

where R is an organic residue containing at least one radical-polymerizable vinyl group; Rc is X or OX where X is a straight-chain, cyclic or branched aliphatic, alicyclic or aromatic hydrocarbon residue containing 1 to 30 carbon atoms, which may optionally be substituted by hydroxyl, halogen, amino or carboxyl or X is a polyether, polyester or polyurethane residue.

3. An adhesive cementing agent as claimed in claim 2 in which the phosphoric or phosphonic acid ester compound is a compound of the general formula:



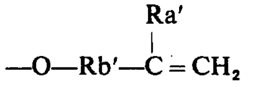
where Ra is hydrogen or methyl; Rb is COOY, OCOY, OY, Y, $CO(OCH_2CH_2)_m$,



$$\mathrm{CO(OCH}\underset{\displaystyle \mathrm{CH_3}}{\underset{|}{\mathrm{C}}}\mathrm{HCH_2)_m},$$

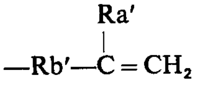
$CO(OCH_2CH_2)_k—O—C_6H_5$ where Y is a straight-chain, cyclic or branched aliphatic, aromatic or alicyclic hydrocarbon residue containing 1 to 30 carbon atoms, which residue may optionally be substituted by hydroxyl, alkoxy or halogen; Rc is as defined in claim 2, *m* is 1, 2, 3, 4 or 5 and *k* is 1, 2 or 3.

4. An adhesive cementing agent as claimed in claim 2 or 3 in which Rc is



$$—O—Rb'—\overset{\displaystyle Ra'}{\overset{|}{C}}=CH_2$$

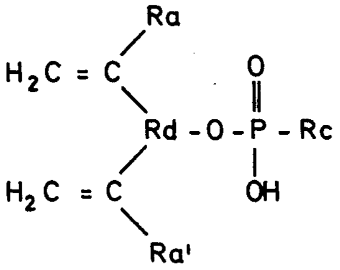
or



$$—Rb'—\overset{\displaystyle Ra'}{\overset{|}{C}}=CH_2$$

where Ra′ and Rb′ are radicals of the type defined for Ra and Rb, respectively, in claim 3.

5. An adhesive cementing agent as claimed in claim 2 in which the phosphoric or phosphonic acid ester compound has the general formula:



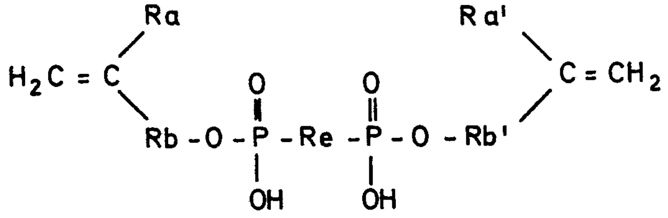
where Ra and Rc are as defined in claim 3; Ra′ is as defined in claim 4, and Rd is

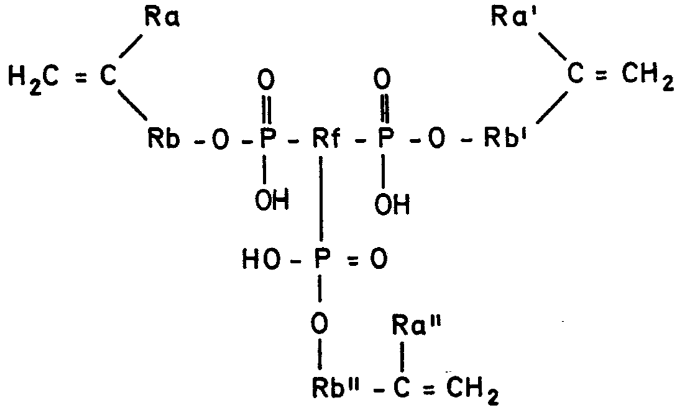
$$—\underset{|}{\mathrm{Y}}—,\quad —\mathrm{O}\underset{|}{\mathrm{Y}}—,\quad —\mathrm{O}\underset{|}{\mathrm{Y}}\mathrm{O}—,\quad —\mathrm{OCO}\underset{|}{\mathrm{Y}}—,\quad —\mathrm{OCO}\underset{|}{\mathrm{Y}}\mathrm{O}—,\quad —\mathrm{OCO}\underset{|}{\mathrm{Y}}\mathrm{COO}—,$$

$$—\mathrm{COO}\underset{|}{\mathrm{Y}}—\quad —\mathrm{COO}\underset{|}{\mathrm{Y}}\mathrm{O}—,\quad —\mathrm{COO}\underset{|}{\mathrm{Y}}\mathrm{COO}— \text{ or } —\mathrm{COO}\underset{|}{\mathrm{Y}}\mathrm{OCO}—$$

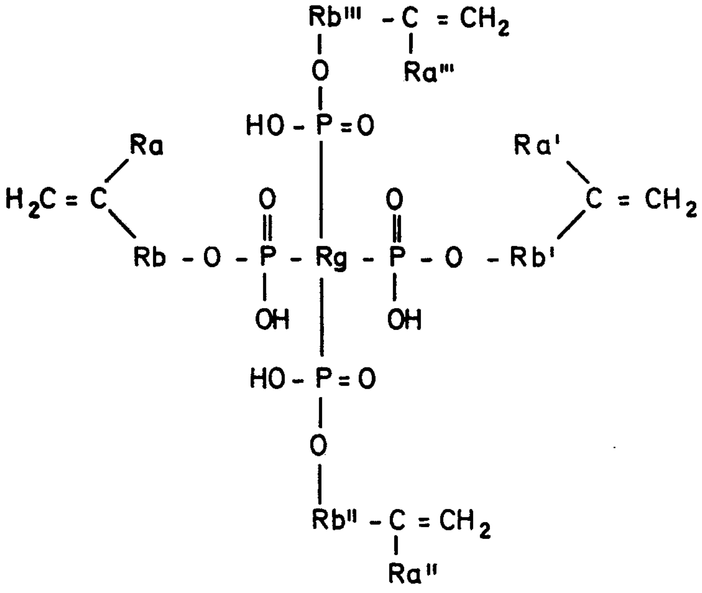
where Y is as defined in claim 3.

6. An adhesive cementing agent as claimed in claim 1 in which the phosphoric or phosphonic acid compound has the general formula:

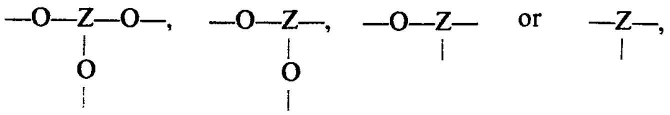




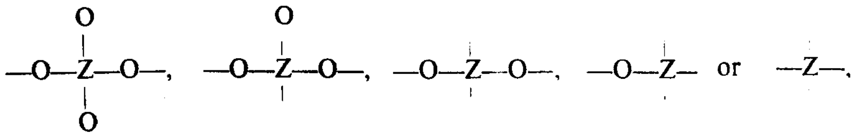
or



where Ra and Rb are as defined in claim 3, Ra′, Ra″ and Ra‴ are radicals of the type defined for Ra; Rb′, Rb″, and Rb‴ are radicals of the type defined for Rb; Re is —O—Z—O—, —O—Z— or —Z—, Rf is



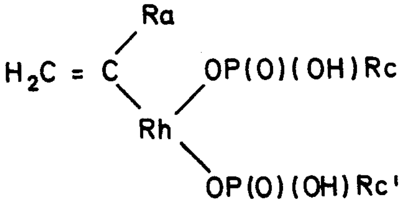
$$-O-\underset{\substack{|\\ O\\ |}}{Z}-O-,\quad -O-\underset{\substack{|\\ O\\ |}}{Z}-,\quad -O-\underset{|}{Z}-\quad \text{or}\quad -\underset{|}{Z}-,$$

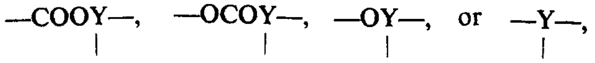
and Rg is 

$-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{Z}}-O-$, $-O-\underset{|}{\overset{\overset{O}{|}}{Z}}-O-$, $-O-\underset{|}{\overset{|}{Z}}-O-$, $-O-\underset{|}{\overset{|}{Z}}-$ or $-Z-$,

where Z is a radical of the type defined for X in claim 2.

7. An adhesive cementing agent as claimed in claim 1 in which said phosphoric or phosphonic acid ester compound has the general formula:



where Rh is 

$-COO\underset{|}{Y}-$, $-OCO\underset{|}{Y}-$, $-O\underset{|}{Y}-$, or $-\underset{|}{Y}-$,

Ra, Rc and Y are as defined in claim 3 and Rc' is a radical of the type defined for Rc in claim 3.

8. An adhesive cementing agent as claimed in claim 1, in which component (a) is a high-molecular-weight compound obtainable by copolymerizing the said phosphoric and/or phosphonic ester compound with an acrylic or methacrylic acid ester compound.

9. An adhesive cementing agent as claimed in any one of claims 1 to 8 in which the radical-copolymerizable comonomer is a comonomer comprising an acrylic or methacrylic acid ester compound.

10. An adhesive cementing agent as claimed in claim 1, in which the phosphoric or phosphonic acid ester compound is any one of those specifically mentioned in the foregoing descriptive part of the specification.

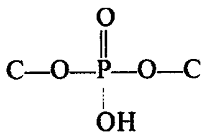
11. An adhesive cementing agent as claimed in claim 9, in which the acrylic or methacrylic acid ester compound is methyl acrylate, ethyl acrylate, hydroxyethyl acrylate, hydroxypropyl acrylate, ethylene glycol diacrylate, (di, tri or tetra)-ethylene glycol diacrylate, neopentyl glycol diacrylate, bisphenol-A diacrylate, 2,2'-bis-(acryloxyethoxyphenyl)propane, 2,2'-bis-(γ-acryloxy-β-hydroxy-propoxyphenyl)propane, 2,2'-bis-(4-acryloxy-propoxyphenyl)propane, xylene glycol diacrylate, trimethylolpropane triacrylate, N,N'-dimethylaminoethyl acrylate or glycidyl acrylate, or the methacrylate corresponding to any of the above.

12. An adhesive cementing agent as claimed in claim 11, in which the curing agent is of the room-temperature-cure type.

13. An adhesive cementing agent as claimed in claim 12, made up into at least two independent packages.

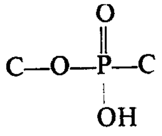
14. An adhesive cementing agent as claimed in claim 1, substantially as hereinbefore described in any one of the Examples.

15. A dental restorative material comprising (A) a filler and (B) a binding component comprising (a) a phosphoric and/or phosphonic acid ester compound containing at least one radical-polymerizable vinyl group and at least one



$C-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-O-C$

or



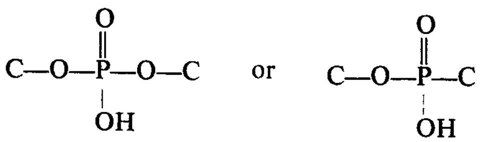
$C-O-\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}-C$

bond, (b) a radical-polymerizable comonomer and (c) a curing agent, in which the weight of phosphorus of component (a) is not less than 0.1% of the weight of the binding component in actual use.

16. A dental restorative material as claimed in claim 15, in which the phosphoric acid ester compound is a compound as defined in any one of claims 2 to 8.

17. A dental restorative material as claimed in claim 15 or 16, in which the radical-copolymerizable comonomer is a comonomer comprising an acrylic or methacrylic acid ester compound.

18. A dental restorative system that comprises a dental filling material comprising a filler, a monomer and a curing agent, and a dental adhesive agent comprising (a) a phosphoric and/or phosphonic acid ester compound containing at least one radical polymerizable vinyl group and at least one



$$\mathrm{C{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}O{-}C} \quad \text{or} \quad \mathrm{C{-}O{-}\underset{\underset{OH}{|}}{\overset{\overset{O}{\|}}{P}}{-}C}$$

bond, (b) a radical polymerizable comonomer and (c) a curing agent, in which the weight of phosphorus of component (a) is not less than 0.1% of the weight of the dental adhesive agent in actual use.

19. A dental restorative system as claimed in claim 18, in which the phosphoric or phosphonic acid ester compound is a compound as defined in any one of claims 2 to 8.

20. A dental restorative system as claimed in claim 18, in which the radical polymerizable comonomer is a compound comprising an acrylic or methacrylic acid ester compound.

21. A dental restorative system as claimed in claim18, in which the phosphoric or phosphonic acid ester compound is dissolved in a volatile organic solvent having a boiling point below 80°C or a comonomer comprising a methacrylic acid ester compound.

22. A dental restorative system as claimed in claim 21, in which the volatile organic solvent is ethanol, diethyl ether or chloroform.

23. A dental restorative system as claimed in claim 21, in which the methacrylic acid ester compound in the dental adhesive agent is methyl methacrylate, 2-hydroxyethyl methacrylate, 3-hydroxypropyl methacrylate, bisphenol-A diglycidyl methacrylate, bisphenol-A dimethacrylate, neopentyl glycol dimethacrylate, ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, or trimethylolpropane trimethacrylate.

24. A dental restorative system as claimed in claim 18, in which the curing agent in the dental adhesive agent is of the room-temperature cure type.

25. A dental restorative system as claimed in claim 24, in which the dental adhesive agent is made up into at least two independent packages.

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