

TABLE I-continued

Example Number	Polymerizable monomer	Sulfur compound (weight %)	Photoinitiator (weight %)	Peroxide Compound (weight %)	Bond Strength, kg/cm <sup>2</sup>	
					One-step	Two-step
24	Example 1	(3) Example 1	(0.15) 2-chloroanthone	(2) —	62.2	63.5
25	Example 1	(3) Example 1	(0.15) 10-methyl-9(10H)acridone	(2) BP	70.5	76.6
26	Example 1	(3) Example 1	(0.15) 10-methyl-9(10H)acridone	(2) —	—	69.8
27	"Clearfil" resin <sup>b</sup>	(3) Example 1	(0.15) 2-chloroanthone	(2) BP	35.0	80.1
28	"Sankin" resin <sup>c</sup>	para-toluene sulfonic acid (5)	(0.15) 2-chloroanthone	(2) BP	—	21.2

<sup>a</sup> Benzoyl peroxide

<sup>b</sup> "Clearfil Bond System F" catalyst liquid (commercially available from Kuraray Co., Ltd.), believed to contain two weight percent benzoyl peroxide in a mixture of monomers including 2-methacryloxyethyl phenyl phosphate, BIS-GMA and triethyleneglycol dimethacrylate.

<sup>c</sup> "Sankin" catalyst liquid (manufactured by Sankin Kogyo Co.), believed to contain one weight percent benzoyl peroxide in  $[(CH_2=C(CH_3)COOC_2H_5)_2P(O)]_2O$ .

These examples show the use of a variety of types and amounts of free-radically polymerizable monomers, sulfur compounds, and photoinitiators in compositions of the invention, with and without a peroxide compound and with one-step and two-step cure methods. Many of these compositions exhibit exceptional increases in bond strength when two-step and one-step cure methods are compared.

#### COMPARISON EXAMPLE

The effect of removal of the sulfur compound and its replacement by an amine was demonstrated as follows. The first part of the non-peroxide-containing composition of Example 1 was combined with a second part containing 0.25 weight percent 2-chloroanthone and 0.5 weight percent diethylaminoethyl methacrylate in absolute ethanol. When the resulting composition was evaluated as in Example 1, the average measured shear strength of the primer-dentin bond was 18.9 kg/cm<sup>2</sup>, a value only 38 percent of the value obtained (49.3 kg/cm<sup>2</sup>) for the sulfur compound-containing composition of Example 1.

In a second comparison, the first part of the non-peroxide-containing composition of Example 9 was combined with a second part containing 0.5 weight percent fluorenone and 0.5 weight percent diethylaminoethyl methacrylate in absolute ethanol. When the resulting composition was evaluated as in Example 9, the average measured shear strength of the primer-dentin bond was 5.2 kg/cm<sup>2</sup>, a value only 9 percent of the value (60.6 kg/cm<sup>2</sup>) obtained for the sulfur compound-containing composition of Example 9.

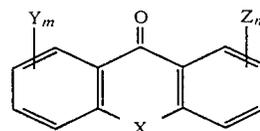
Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not limited to the illustrative embodiments set forth herein.

We claim:

1. A visible light cure dentin and enamel primer composition, comprising:

- (a) as a first component, phosphorous-containing free-radically polymerizable monomer suitable for use in the oral environment;
- (b) as a second component, sulfur compound having sulfur in the +2 or +4 oxidation state, said second component acting as a polymerization activator for said first component and enhancing adhesion of said composition to dentin; and

(c) as a third component, photoinitiator selected from substituted and unsubstituted alkylphenones, substituted and unsubstituted benzilidene acetophenones, and compounds of the formula:



wherein:

X is nothing, a carbon-carbon bond, CR<sub>2</sub>, C=I, C=O, S, SO, SO<sub>2</sub>, O, or NR where each R is independently H or a lower alkyl or substituted alkyl group and R<sup>1</sup> is a tetravalent unsaturated aliphatic radical doubly bonded to said C of C=R<sup>1</sup> and bonded to the 4 or 5 position of said Formula I to form a fused ring structure;

Y and Z are independently lower alkyl, substituted alkyl, a divalent unsaturated radical bonded to adjacent positions of said Formula I to form a fused ring structure, alkoxy, halogen, or nitro; and

m and n are independently zero to 4.

2. A composition according to claim 1, wherein said polymerizable monomer contains phosphorus atoms bonded to one or more olefinically unsaturated groups and bonded to one or more chlorine atoms, bromine atoms, active hydrogen atoms, or alkyl, substituted alkyl, allyl, or substituted allyl groups.

3. A composition according to claim 1, wherein said polymerizable monomer comprises an organic ester of one or more acids of phosphorus, the organic radical of said ester containing at least one free-radically polymerizable functional group, and wherein said ester has chlorine or bromine bonded directly to phosphorus.

4. A composition according to claim 1, wherein said polymerizable monomer is selected from

- (a) 2-methacryloxyethyl phenyl phosphate, and
- (b) halophosphorus ester wherein the organic radical of said ester is the residue remaining after removal of one or more hydroxyl hydrogen atoms from BIS-GMA, phosphorus is doubly bonded to an oxygen atom, is bonded to at least one chlorine atom, and the ratio of said phosphorus to said BIS-GMA is between about 0.015:1 and 1:1.