

LIGHT-CURABLE DENTIN AND ENAMEL ADHESIVE

TECHNICAL FIELD

This invention relates to light-curable compositions useful in dentistry. This invention also relates to a method for repairing, adhering to, or altering the position of teeth, through the use of such compositions.

BACKGROUND ART

Practitioners in the field of dentistry have long sought polymerizable compositions which would adhere well to dentin. A number of compositions having varying degrees of adhesion to dentin have been reported in the literature, see, e.g., M. Buonocore, W. Wileman, and F. Brudevold, *J. Dent. Res.*, 35, 846 (1956), M. Buonocore and M. Quigley, *J. Amer. Dent. Assoc.*, 57, 807 (1958), M. Anbar and E. Farley, *J. Dent. Res.*, 53, 879 (1974), E. Farley, R. Jones, and M. Anbar, *J. Dent. Res.*, 56, 1943 (1977), R. L. Bowen, E. N. Cobb, and J. E. Rapson, *J. Dent. Res.*, 61, 1070 (1982), R. L. Bowen, E. N. Cobb, and L. E. Setz, *Dentistry* 82, 11 (December 1982), U.S. Pat. Nos. 4,182,035, 4,222,780, 4,235,633, 4,259,075, 4,259,117, and 4,368,043, European published patent application No. 0 058 483, and Japanese laid-open patent application (Kokai) Nos. 57-143372 and 57-167364. These compositions generally are used in the form of primers or liners which are applied to dentin in one or more thin coats followed by application of a dental composite, restorative, or adhesive composition to the primer-coated dentin surface.

In recent years, one-part visible light cure compositions have become popular in dentistry, particularly in connection with dental composite, restorative, and adhesive compositions, as these compositions typically are highly loaded with fillers and are difficult to mix with chemical cure polymerization initiators. There has been no particularly pressing need for one-part visible light cured dentin primers, since such primers are low viscosity liquids containing little or no filler content, and can be readily dispensed, mixed, and used in conventional two-part chemical cure formats. There has been relatively little discussion in the literature of visible light cure dentin primers, exceptions being the above-mentioned European patent application No. 0 058 483 (which describes a light-cured dentin primer containing photoinitiators "such as monoketals of aromatic 1,2-diketones or a combination of benzil and a dialkylamino acrylate or methacrylate"), and Japanese laid-open patent application No. 56-120610 (abstracted in *Chem. Abs.*, 95, 225704u (1981)), and said to describe a resin mixture containing diglycidyl methacrylate of Bisphenol A (also known as "BIS-GMA"), triethylene glycol dimethacrylate and 2-methacryloxyethyl phenyl phosphate, which mixture is polymerized in the presence of camphoroquinone and allylthiourea.

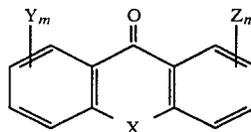
Many references describe one-part visible light cure compositions which contain fillers and are suitable for use in dentistry, including U.S. Pat. Nos. 3,709,866 and 4,110,184, and European published patent application Nos. 0 059 649, 0 058 483, and 0 070 634. Other visible light cure compositions said to have more general utility (e.g., as paints or coatings) are disclosed in U.S. Pat. Nos. 3,759,807, 3,926,643, 4,071,424, and 4,089,762. Most of the visible light cure compositions exemplified in the above-mentioned references contain an amine compound which facilitates photopolymerization.

Some of the above-mentioned references suggest other compounds which can be used in place of an amine; one reference (U.S. Pat. No. 4,110,184) mentions (without exemplifying) the use of "soluble salts of aromatic sulfonic acids" in place of amines in a filler-loaded visible light cure dental composition.

DISCLOSURE OF INVENTION

The present invention provides, in one aspect, two-part visible light cure dentin and enamel primer compositions. When said two parts are mixed, said compositions comprise:

- (a) phosphorus-containing free-radically polymerizable monomer suitable for use in the oral environment;
- (b) sulfur compound having sulfur in the +2 or +4 oxidation state; and
- (c) Photoinitiator selected from substituted (e.g., with lower (C₁₋₄) alkyl, substituted alkyl, alkoxy, halogen, or nitro) and unsubstituted alkylphenones, substituted (e.g., with lower (C₁₋₄) alkyl, unsubstituted alkyl, alkoxy, halogen, or nitro) and substituted benzilidene acetophenones, and compounds of the formula:



wherein:

X is nothing (i.e., not bond), a carbon-carbon bond, $>CR_2$, $>C=R^1$, $>C=O$, $>S$, $>SO$, $>SO_2$, $>O$, or $>NR$ where each R is independently H or a lower (C₁₋₄) alkyl or substituted alkyl group and R¹ is a tetravalent unsaturated aliphatic radical doubly bonded to said C of $>C=R^1$ and bonded to the 4 or 5 position of said Formula I to form a fused ring structure;

Y and Z are independently lower (C₁₋₄) alkyl, substituted alkyl (e.g., $-CF_3$), a divalent unsaturated radical bonded to adjacent positions of said Formula II to form a fused ring structure, alkoxy, halogen, or nitro; and

m and n are independently zero to 4.

The present invention also provides a method for using such compositions to repair or veneer hard dental tissue, and a method for applying orthodontic brackets or crowns to hard dental tissue using said compositions.

The compositions of the invention are two-part visible light cure compositions, in contrast to typical light cure compositions which are packaged as one-part systems. Two-part packaging is used in the present invention since the sulfur compound (viz., component (b), above) tends to promote homopolymerization of the phosphorus-containing polymerizable monomer (viz., component (a), above) if components (a) and (b) are stored together. The two parts (one part containing component (a), the other part containing component (b), and one or both parts containing component (c)) are mixed together just prior to use, applied to dentin or enamel, and irradiated with a conventional visible light source. Although the use of a two-part visible light cure composition may seem to be a step backward from the standpoint of convenience (since an ordinary two-part chemical cure composition would be just as easily mixed and would not require use of a curing light), the compositions of the invention nonetheless represent a