

the two systems is in the second component, the adhesive monomer component or composition (B2). The adhesive monomer composition (B2) of the second etchant/primer/adhesive monomer system (B) differs from (A2) in that it contains a monomer system without the conventional free-radical initiator and may also include no accelerator, other than those discussed below. Like the etchant/primer/adhesive monomer system (A), the system (B) may employ separately packaged (i.e., in separate containers) components (B1) and (B2). The components (B1) and (B2) may each contain their own solvent systems, which are the same or are miscible with one another and compatible with the separate solutes. Where only one of the components, the etchant/primer compound(s) or the adhesive monomer(s) is dissolved in a solvent system, the solvent should be one suitable for dissolving the other components of the system.

In use, the (B) system may be used according to one of two different methods according to the present invention. Thus, the first method is identical to the method employed with the (A) system. That is, a solution of (B1) is applied to the substrate, typically dentin, and either lightly rinsed with water or left unrinsed. Thereafter, a solution of the adhesive monomer (B2) is applied to the substrate surface and polymerization and curing allowed to take place. Because of the initiating and accelerating properties of the etchant/primer compositions of the present invention, the absence of an initiator in (B2) presents no problem in rapid polymerization, particularly when highly active monomers of the type discussed above, such as those which include acid, hydroxyl, amine or quaternary ammonium groups are used, or when an activating cation is present.

In the second method of using the etchant/primer/adhesive monomer systems (B), the steps of etching, priming and forming an adhesive polymer may be accomplished in a single step. Thus, the separate components (B1) and (B2), including the substances described above, may be combined in a single solution and applied to the substrate. In this method, rather than sequentially applying separate solutions, a single solution containing the etchant/primer compound and the solvent system of the present invention as well as the monomer system, and generally without a conventional free-radical initiator, is applied as a single solution. In such an instance, either (B1) or (B2) may be solvent-free, with the other of the components containing a solvent system suitable for dissolving the solvent-free component. Alternatively, both components may include a suitable solvent system which is compatible with the solvent system of the other component.

What is claimed is:

1. A method for preparing a dental or other substrate surface for adhesion of a polymeric material comprising contacting the surface with an etchant/primer/adhesive monomer composition comprising:

a compound having the formula



wherein

$\text{R}=\text{R}^1$ or R^2 ;

R^1 =an aromatic group;

R^2 =a conjugated aliphatic group;

Y =a single bond, CH_2 , CHCH_3 or $\text{C}=\text{CH}_2$; and each M is independently H, an alkali metal, an alkaline earth metal, aluminum, a transition or redox metal or an alkyl group having 1 to 18 carbon atoms, with the proviso that when both M groups are alkyl groups, the com-

pound corresponding to formula I be capable of being easily hydrolyzed, displaced, or exchanged with other reagents present in the etchant/primer composition; and a polar solvent.

2. A method according to claim 1 wherein said polar solvent system comprises an aqueous solvent.

3. A method according to claim 2 wherein said aqueous solvent comprises water and acetone.

4. A method according to claim 1 wherein R^1 comprises C_6H_5 or $\text{C}_6\text{H}_4\text{R}^3$, and

wherein $\text{R}^3=\text{N}(\text{CH}_2\text{CO}_2\text{M})_2$; $\text{C}_6\text{H}_4\text{N}(\text{CH}_2\text{CO}_2\text{M})_2$; $\text{O}(\text{CH}_2)_2\text{OC}_6\text{H}_4\text{N}(\text{CH}_2\text{CO}_2\text{M})_2$; $\text{CH}=\text{CH}_2$; CO_2H ; F ; Cl ; Br ; I ; OH ; SH ; (m- or p-) $\text{CH}_2\text{C}_6\text{H}_4$ (m- or p-) $\text{CH}=\text{CH}_2$; $\text{OCOC}(\text{R}^4)=\text{CH}_2$; $\text{NR}^4\text{COC}(\text{R}^4)=\text{CH}_2$; $(\text{CH}_2)_2\text{OCOC}(\text{R}^4)=\text{CH}_2$; C_6H_5 ; an alkyl group having 1 to 12 carbon atoms; HOCH_2 ; HOCH_2CH_2 ; R^5_2N ; R^6O ; R^6S ; R^6CO ; R^7CONH ; R^7COCO ,

wherein $\text{R}^4=\text{H}$ or CH_3 ;

wherein $\text{R}^5=\text{H}$ or an alkyl group having 1 to 8 carbon atoms;

wherein R^6 =an alkyl group having from 1 to 6 carbon atoms; and

wherein R^7 =an alkyl group having 1 to 6 carbon atoms.

5. A method according to claim 1 wherein said compound of formula (I) is phenyliminodiacetic acid, a salt thereof or an ester thereof.

6. A method according to claim 1 wherein R^2 comprises a residue of crotonic acid, a salt thereof or an ester thereof.

7. A method for forming a polymeric material at and a strong integrated bond with a dental or other substrate surface comprising:

(a) contacting the surface with an etchant/primer composition comprising:

a compound having the formula



wherein

$\text{R}=\text{R}^1$ or R_2 ;

R^1 =an aromatic group;

R^2 =a conjugated aliphatic group;

Y =a single bond, CH_2 , CHCH_3 or $\text{C}=\text{CH}_2$; and

each M is independently H, an alkali metal, an alkaline earth metal, aluminum, a transition or redox metal or an alkyl group having 1 to 18 carbon atoms, with the proviso that when both M groups are alkyl groups, the compound corresponding to formula I be capable of being easily hydrolyzed, displaced, or exchanged with other reagents present in the etchant/primer composition, and

a polar solvent system to form a conditioned and primed surface;

(b) applying to said conditioned and primed surface an adhesive monomer system; and

(c) curing said adhesive monomer system.

8. A method according to claim 7 wherein said polar solvent system comprises an aqueous solvent.

9. A method according to claim 8 wherein said aqueous solvent comprises water and acetone.

10. A method according to claim 7 wherein R^1 comprises C_6H_5 or $\text{C}_6\text{H}_4\text{R}^3$, and

wherein $\text{R}^3=\text{N}(\text{CH}_2\text{CO}_2\text{M})_2$; $\text{C}_6\text{H}_4\text{N}(\text{CH}_2\text{CO}_2\text{M})_2$; $\text{O}(\text{CH}_2)_2\text{OC}_6\text{H}_4\text{N}(\text{CH}_2\text{CO}_2\text{M})_2$; $\text{CH}=\text{CH}_2$; CO_2H ; F ; Cl ; Br ; I ; OH ; SH ; (m- or p-) $\text{CH}_2\text{C}_6\text{H}_4$ (m- or p-) $\text{CH}=\text{CH}_2$; $\text{OCOC}(\text{R}^4)=\text{CH}_2$; $\text{NR}^4\text{COC}(\text{R}^4)=\text{CH}_2$;