

3

These and other objects are accomplished by the embodiments described below. One embodiment of the present invention comprises an etchant/primer composition comprising:

a compound having the formula:



wherein  $\text{R}=\text{R}^1$  or  $\text{R}^2$ ;  
 $\text{R}^1$ =an aromatic group;  
 $\text{R}^2$ =a conjugated unsaturated aliphatic group;  
 $\text{Y}$ =a single bond,  $\text{CH}_2$ ,  $\text{CHCH}_3$  or  $\text{C}=\text{CH}_2$ ; and  
 each  $\text{M}$  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  $\text{M}$  groups are alkyl groups, the compound is capable of being easily hydrolyzed, displaced, or exchanged with other reagents present in the etchant/primer composition;

a polar solvent system; and

nitric acid.

According to another embodiment, a method of preparing a dental substrate for contact with an adhesive resin or an adhesive resin monomer is provided. This method comprises the step of contacting the substrate with an etchant/primer composition that comprises:

a compound having the formula:



wherein  $\text{R}=\text{R}^1$  or  $\text{R}^2$ ;  
 $\text{R}^1$  an aromatic group;  
 $\text{R}^2$ =a conjugated unsaturated aliphatic group;  
 $\text{Y}$ =a single bond,  $\text{CH}_2$ ,  $\text{CHCH}_3$  or  $\text{C}=\text{CH}_2$ ; and  
 each  $\text{M}$  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  $\text{M}$  groups are alkyl groups, the compound is capable of being easily hydrolyzed, displaced, or exchanged with other reagents present in the etchant/primer composition;

a polar solvent system; and

nitric acid.

Other embodiments of the claimed invention are described below.

#### DETAILED DESCRIPTION OF THE INVENTION

Broadly, the etchant/primer composition in accordance with the present invention comprises an aryl- or alkenyl-iminodiacetic acid (or derivative thereof), a polar solvent system and nitric acid. Further, in general, the etchant/primer/adhesive monomer composition in accordance with the present invention comprises such iminodiacetic acids (or derivatives thereof), a polar solvent system, an acid, and an adhesive monomer.

The Iminodiacetic Acid

According to one embodiment, the etchant/primer composition of the present invention comprises a compound of formula (I):



a polar solvent system and nitric acid. The compound of formula (I) is an iminodiacetic acid or a derivative thereof (the term "iminodiacetic acid" as used herein is intended to

4

mean the acid itself or its derivatives) wherein  $\text{R}=\text{R}^1$  or  $\text{R}^2$ ;  $\text{R}^1$ =an aromatic group;  $\text{R}^2$ =a conjugated unsaturated aliphatic group;  $\text{Y}$ =a single bond,  $\text{CH}_2$ ,  $\text{CHCH}_3$  or  $\text{C}=\text{CH}_2$ ; and each  $\text{M}$  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  $\text{M}$  groups are alkyl groups, said compound is capable of being easily hydrolyzed, displaced, or exchanged with other reagents present in the etchant/primer composition. An example of an easily hydrolyzed group is t-butyl.

$\text{R}^1$  may be a heterocyclic aromatic group. Preferably,  $\text{R}^1$  is a carbocyclic aromatic group, particularly a phenyl or naphthyl group or derivatives thereof. Most preferred  $\text{R}^1$  groups are substituted and unsubstituted phenyl groups. When substituted, the substituents may be electron donating or electron withdrawing and located at either the ortho, meta or para positions of the phenyl ring. However, when the substituent is of a sufficient size to impart steric hindrance, it is preferred that the substituent be located at the meta or para position. Preferred substituents are groups which are the same or similar to the iminodiacetic acid group or derivatives thereof which extend the conjugated system of the aromatic ring.

In the present invention,  $\text{R}^1$  is preferably  $\text{C}_6\text{H}_5$  or  $\text{C}_6\text{H}_4\text{R}^3$ , wherein  $\text{R}^3=\text{N}(\text{CH}_2\text{CO}_2\text{M})_2$ ;  $\text{C}_6\text{H}_4\text{N}(\text{CH}_2\text{CO}_2\text{M})_2$ ;  $\text{R}^4\text{O}(\text{CH}_2)_2\text{OC}_6\text{H}_4\text{N}(\text{CH}_2\text{CO}_2\text{M})_2$ ;  $\text{CH}=\text{CH}_2$ ;  $\text{CO}_2\text{H}$ ; F; Cl; Br; I; OH; SH; (m- or p-)  $\text{CH}_2\text{C}_6\text{H}_4$ (m- or p-)  $\text{CH}=\text{CH}_2$ ;  $\text{OCOC}(\text{R}^4)=\text{CH}_2$ ;  $\text{NR}^4\text{COC}(\text{R}^4)=\text{CH}_2$ ;  $(\text{CH}_2)_2\text{OCOC}(\text{R}^4)=\text{CH}_2$ ;  $\text{C}_6\text{H}_5$ ; an alkyl group having 1 to 12 carbon atoms;  $\text{HOCH}_2$ ;  $\text{HOCH}_2\text{CH}_2$ ;  $\text{R}^5\text{N}$ ;  $\text{R}^6\text{O}$ ;  $\text{R}^6\text{S}$ ;  $\text{R}^6\text{CO}$ ;  $\text{R}^7\text{CONH}$ ;  $\text{R}^7\text{COCO}$ , wherein  $\text{R}^4=\text{H}$  or  $\text{CH}_3$ ; wherein each  $\text{R}^5$  is independently H or an alkyl group having 1 to 8 carbon atoms and is preferably  $\text{CH}_3$ , or  $\text{C}_2\text{H}_5$ ; wherein  $\text{R}^6$ =an alkyl group having from 1 to 6 carbon atoms, preferably  $\text{CH}_3$ ; and wherein  $\text{R}^7$ =an alkyl group having 1 to 6 carbon atoms, preferably  $\text{CH}_3$  or  $\text{CH}_2\text{CH}_3$ . Suitable for use as  $\text{R}^1$  are also various derivatives of p-2-hydroxyethylphenyliminodiacetic acid or soluble salts thereof, such as  $\text{R}^8(\text{p-NHCOO}(\text{CH}_2)_2\text{C}_6\text{H}_4\text{N})\text{CH}_2\text{CO}_2\text{M})_2$  wherein  $\text{R}^8$  is an alkyl group.

In the present invention,  $\text{R}^2$  may be an unsaturated cycloaliphatic group, or more preferably, a linear or branched unsaturated aliphatic group, such exemplary aliphatic groups include carbon-to-carbon bonds, carbon-to-nitrogen bonds, or combinations thereof, which are conjugated, unsaturated bond(s). Within the aliphatic group may be other atoms such as N or O which are part of ester, carbonyl, ether, amino, imino, or amide groups or combinations thereof. The number of carbon atoms present within  $\text{R}^2$  ranges from 4 to 20.

Preferably,  $\text{R}^2$  includes one or more vinyl groups. Most preferably,  $\text{R}^2$  includes a residue of crotonate ( $\text{CH}_3\text{CH}=\text{CHCO}_2\text{M}$ ) or substituted crotonate groups present as the free acid, ester or salt of the type described herein for iminodiacetic acid salts. Preferred crotonate derivatives are those in which bonding to the nitrogen atom of the iminodiacetic acid group takes place either through the carbon atom number 2 or carbon atom number 3 of the crotonate residue, with the latter being the most preferred. In such an instance,  $\text{R}^2$  represents  $\text{CH}_3\text{C}=\text{CHCO}_2\text{R}^9$ .  $\text{R}^9$  represents M, wherein M has the same meaning as indicated above, including a vinyl group or an alkyl group having from 1 to 24 carbon atoms, preferably  $\text{CH}_3$  or  $\text{CH}_2\text{CH}_3$ . Other preferred  $\text{R}^2$  groups include the residue of cinnamic acid, present as the free acid, ester or its salt.

Iminodiacetic acids suitable for use in conjunction with the present invention include, but are not limited to, m- or