p-vinyl-N-phenyliminodiacetic acid; N-p-acrylphenyliminodiacetic acid; methacrylamidophenyliminodiacetic acid; N,N-(carboxymethyl-2-carboxyallyl) aniline; N,N-bis(2-carboxyallyl)aniline; m- or p-vinyl, m- or p-benzyl-N-phenyliminodiacetic acid; N,N,N'N'-p-phenylenediaminotetraacetic acid; N,N'-(1,2-ethanediyl bis (oxy-2,1-phenylene)-bis-N-carboxymethyl) (also known as 1,2-bis(o-aminophenoxy-)ethane-N,N,N',N'-tetraacetic acid or BAPTA); o-, m-, or p-biphenylenediiminodiacetic acid; carboxy-N-phenyliminodiacetic acid; N-phenyliminodiacetic acid; and combinations thereof. The most preferred iminodiacetic acid is PIDAA, salts and esters thereof. Suitable examples of PIDAA salts include the dipotassium and magnesium salts thereof.

Many of the compounds of formula (I) used in the etchant/primer composition or the etchant/primer/adhesive monomer composition of the present invention are available from commercial sources. Where commercially unavailable, the synthesis of appropriate compounds in which R^1 is an aromatic group, such as a phenyl or a substituted phenyl group, may be achieved by the procedure described in Lin et al., *Synthesis*, 7, pp. 548–49 (July 1998). This method involves reacting the appropriate substituted or unsubstituted aniline with sodium chloroacetate in the presence of n-butyllithium as a base. Many of the compounds according to formula (I) in which $R=R^2$ may be prepared in a similar manner. Many of the olefinic compounds in which $R=R^2$ may be prepared by a method similar to that used to prepare the crotonyl-N-iminodiacetic acid compounds. For example, 3-aminocrotonic acid and its esters can be reacted with haloacetic acid or derivatives thereof, such as chloroacetic acid, to synthesize the analogous N,N-diacetic acid derivatives of crotonic acid, its esters, salts and the like using a mild base in an appropriate solvent. Alternatively, the aromatic or appropriate aliphatic amine may be reacted with haloacetic acid or a derivative thereof. In addition, iminodiacetic acid may be reacted with the appropriate conjugated unsaturated organic halide in an appropriate solvent and in the presence of a base such as triethylamine.

Polar Solvent System

Polar solvent systems suitable for use in conjunction with the present invention comprise water and/or a polar solvent which is partially or totally soluble in water. For dental applications, a suitable solvent system is one which completely wets and diffuses into the surface of the enamel and particularly dentin in a clinically acceptable period of time (on the order of about 15 to about 180 seconds). With reference to wetting and diffusing of the solvent system into enamel or dentin, such wetting and diffusing is preferably to a depth of not more than about 5 microns.

Examples of polar solvents suitable for use in conjunction with the present invention include, but are not limited to, low molecular weight ketones such as acetone and methyl ethyl ketone, low molecular weight alcohols such as propanol or ethanol, polar aprotic solvents such as dimethylformamide, dimethylacetamide, dimethylsulfoxide, 1-methyl-2-pyrrolidinone or combinations and mixtures thereof. Water or a mixed solvent system of water and acetone is preferred. In such a solvent system, the amount, by volume, of acetone may range from about 5% to about 90% acetone with the remainder being water. Preferred is a 1:1 by volume mixture of acetone and water. Water may be used more frequently as a component of the solvent system when the etchant/primer composition includes a water-soluble salt. Small amounts (e.g., about 1% by weight or slightly greater than 1% by weight) of surfactants may be used to enhance the solvent potential of these solvent systems.

The concentration of the iminodiacetic acid within the etchant/primer composition or the etchant/primer/adhesive monomer composition of the present invention may be varied. For example, when the iminodiacetic acid comprises PIDAA and the polar solvent system comprises acetone and water, the concentration of the iminodiacetic acid ranges from about 1% to about 20% by weight, based on a total weight of the etchant/primer composition or the etchant/primer/adhesive monomer composition being applied.

The Acid

The Etchant/Primer Composition

The acid selected should be sufficient to etch the dentin, enamel or other dental structure to facilitate improved adhesion of the adhesive resin or monomer thereto. In addition, the acid should be sufficient to permit the adhesive resin or monomer to wet, infiltrate or penetrate, and to conform to the vital dentinal or enamel substrate. The acid should also be sufficient to strengthen the SBS of the bond between the adhesive resin and the underlying dental structure. Such an acid for use in conjunction with the etchant/primer composition of the present invention is nitric acid.

In addition to the iminodiacetic acid and polar solvent system, the etchant/primer composition further comprises nitric acid provided in an amount, preferably, ranging from about 0.05% to about 5.0% by weight, based on a total weight of the etchant/primer composition. More preferably, the nitric acid is provided in an amount ranging from about 0.1% to about 2.5% by weight, based on a total weight of the etchant/primer composition.

The etchant/primer composition of the present invention is applied to the relevant dental structure for a time sufficient to pre-treat the dental structure prior to application of an adhesive resin, an adhesive resin monomer (containing an initiator e.g., a photo-initiator, a free-radical initiator, or other types of chemical initiator) or combinations thereof. Typically, time periods for applying the etchant/primer composition to the relevant dental structure range from about 15 seconds to about 180 seconds, preferably, from about 30 seconds to about 120 seconds, and most preferably, from about 30 seconds to about 60 seconds.

Etchant/Primer/Adhesive Monomer Composition

The acid selected should be sufficient to etch the dentin, enamel or other dental structure to facilitate improved adhesion of the adhesive resin or monomer thereto. In addition, the acid should be sufficient to permit the adhesive resin or monomer to wet, infiltrate or penetrate, and to conform to the vital dentinal or enamel substrate. The acid should also be sufficient to strengthen the SBS of the bond between the adhesive resin and the underlying dental structure.

Suitable acids for use with the etchant/primer/adhesive monomer composition of the present invention, include, but are not limited to, nitric acid, hydrochloric acid, lactic acid, glycolic acid, formic acid, pyruvic acid, citric acid, and strong acids that form chelating agents or combinations and mixtures thereof.

The acid is typically provided in an amount ranging from about 0.05% to about 5.0% by weight, based on a total weight of the etchant/primer/adhesive monomer composition. Preferably, the acid is provided in an amount ranging from about 0.1% to about 2.5% by weight, based on a total weight of the etchant/primer/adhesive monomer composition.

Initiators

Adhesive resin polymers or adhesive resin monomers for dental restoration, typically include chemical, photochemical or dual-curing free-radical initiators. See, for example,