

water were removed by evaporation until the refractive index was about $n_D^{24}=1.5$ for the clear, light yellow liquid with a sweet, aromatic odor. When this product was used in adhesion tests of the kind described in U.S. Pat. Nos. 4,514,527; 4,521,550; 4,588,756; and 4,659,751, the bond strengths to human dentin averaged 1,410 psi.

It has surprisingly been discovered that compounds containing both a polymerization photoinitiator and/or co-photoinitiator and/or a polymerization inhibitor (stabilizer) and/or a polymerizable group can be prepared by using compounds such as those in the foregoing formulations together with the probability statistics described above, provided that during preparation and storage before use, said compounds are protected from high-energy light, contain stabilizers, and are kept under conditions, such as in plastic containers, where they are not deprived of oxygen.

Additional Example 4

A hydrophilic monomer formulation was prepared by combining 1 mole of pyromellitic dianhydride, with 1.9 moles of glycerol dimethacrylate, GDM, a HM/HA, and a trace of stabilizer, PS, using insoluble poly(vinylpyridine) as a catalyst, at room temperature in dried acetone. When NMR showed apparent depletion of the dianhydride, water was admitted inadvertently, hydrolyzing residual anhydride groups. The catalyst was removed by filtration and the acetone was removed by evaporation. Surprisingly, final NMR analysis indicated a monomeric mixture containing a major proportion of molecules containing 3 carboxyl groups, with 2 methacrylate groups, a minor proportion containing 2 carboxyl groups with 4 methacrylate groups, some residual GDM, and little if any pyromellitic acid. Formulations containing this reaction product gave high tensile adhesive bond strengths to prepared dentin and metallic surfaces.

It should be understood that the foregoing disclosure emphasizes certain specific embodiments of the invention and that all modifications or alternatives equivalent thereto are within the spirit or scope of the invention as set forth in the appended claims.

What is claimed is:

1. A hydrophilic fluid crosslinking adhesive composition comprising reaction products of
 - (a) a dianhydride with
 - (b) a hydrophilic polymerizable monomer compound containing a polymerizable moiety and a reactive group selected from the group consisting of a hydroxyl group, a primary amino group and a secondary amino group; and with
 - (c) a reactive reagent selected from the group consisting of compounds containing a reactive group selected from the group consisting of a hydroxyl group, a primary amino group and a secondary amino group; and also containing a functional group selected from the group consisting of (a) one or more compounds containing one reactive hydroxyl group, or primary or secondary amino group, a cophotoinitiator functionality, a polymerization accelerator functionality, and a polymerization stabilizer functionality,

wherein the compounds of subparts (a), (b) and (c) are reacted in molar ratios of about 1:1.55-1.99:0.01-0.45, respectively, to provide the reaction products, and wherein the reaction products have similar aqueous solubility and surface activity characteristics.

2. A composition as in claim 1 wherein the dianhydride of subpart (a) comprises a eutectic mixture of dianhydrides.

3. A composition as in claim 1 wherein the dianhydride of subpart (a) is selected from the group consisting of *s*-biphenyl tetracarboxylic acid dianhydride, glycerol acetate bistrimellitate dianhydride, 3,3',4,4'-diphenylsulfone tetracarboxylic acid dianhydride, 4,4'-oxydiphthalic dianhydride, 4,4'-(hexafluoroisopropylidene)-bispthalic anhydride, pyromellitic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, ethylene glycol bistrimellitate dianhydride, 5-(2,5-dioxotetrahydro-3-furanyl)-3-cyclohexene-1,2-dicarboxylic anhydride, 1,2,3,4-cyclopentane tetracarboxylic acid dianhydride, mellophanic dianhydride, bicyclo(2,2,2)octane-2,3,5,6-tetracarboxylic dianhydride, bicyclo(2,2,2)-7-octene-2,3,5,6-tetracarboxylic dianhydride, and mixtures thereof.

4. A composition as in claim 1 wherein the solubility of the composition in water is at least 1%.

5. A composition as in claim 2 wherein the dianhydride of subpart (a) is selected from the group consisting of *s*-biphenyl tetracarboxylic acid dianhydride, glycerol acetate bistrimellitate dianhydride, 3,3',4,4'-diphenylsulfone tetracarboxylic acid dianhydride, 4,4'-oxydiphthalic dianhydride, 4,4'-(hexafluoroisopropylidene)-bispthalic anhydride, pyromellitic dianhydride, 3,3',4,4'-benzophenone tetracarboxylic dianhydride, ethylene glycol bistrimellitate dianhydride, 5-(2,5-dioxotetrahydro-3-furanyl)-3-cyclohexene-1,2-dicarboxylic anhydride, 1,2,3,4-cyclopentane tetracarboxylic acid dianhydride, mellophanic dianhydride, bicyclo(2.2.2)octane-2,3,5,6-tetracarboxylic dianhydride, bicyclo(2.2.2)-7-octene-2,3,5,6-tetracarboxylic dianhydride, and mixtures thereof.

6. A composition as in claim 1 wherein the polymerizable moiety of the hydrophilic polymerizable monomer compound of subpart (b) is capable of free-radical polymerization.

7. A composition as in claim 1 wherein some of the reaction products contain a polymerizable moiety and a functionality selected from the group consisting of a polymerization cophotoinitiator, a polymerization accelerator and a polymerization stabilizer, located on the same molecule as the polymerizable moiety.

8. A composition as in claim 7 wherein the hydrophilic polymerizable monomer compound of subpart (b) is comprised of molecules that contain a methacrylate or acrylate group connected to a reactive group selected from the group consisting of an unesterified hydroxyl group, a primary amino group and a secondary amino group, said groups connected by a connecting moiety, the connecting moiety selected from the group consisting of $-\text{CH}_2-$ groups, $-\text{CH}_2\text{CH}_2\text{O}-$ groups, $-\text{CH}(\text{CH}_3)\text{CH}_2\text{O}-$ groups, $-\text{CH}(\text{CH}_3)\text{CH}_2-$ groups, cyclic aliphatic groups, heterocyclic aliphatic groups and aromatic groups.

9. A composition as in claim 8 wherein the hydrophilic polymerizable monomer compound of subpart (b) is selected from the group consisting of hydroxymethacrylate, hydroxyacrylate, glycerol dimethacrylate, glycol monomethacrylate, polyethylene glycol monomethacrylate, propylene glycol monomethacrylate, oligopropylene glycol monomethacrylate, hydroxypropyl methacrylate, polypropylene glycol monomethacrylate, hydroxyethyl-methacrylate, glycerol diacrylate, 2-tert-butylaminoethyl methacrylate, the reaction prod-