

the partial sodium salt, was applied to dentin surfaces for 60 seconds. The EDTA solution was rubbed on the surface lightly with cotton pledget for about 30 seconds and then the solution was allowed to stand for the additional 30 seconds. The surface was then rinsed with distilled water for 10 seconds, blown with air for 10 seconds, and the 10% acetone solution of NPG was applied, followed by the PMDM solution and the composite as described previously. The average bond strength on dentin of eight teeth was 12.0 MPa (s.d.=3.6). With the same application of the EDTA solution, but with omission of the NPG solution, treatment with the PMDM and composite yielded an average of only 2.6 MPa (s.d.=2.0).

EXAMPLE 5

Other acids can be used in conjunction with NPG and PMDM. For example, an aqueous solution of 35% H₃PO₄ (orthophosphoric acid) combined with 6% NPG was applied to dentin surfaces for 60 seconds, washed with water, blown with air, and then an acetone solution of PMDM was applied as before. The average of eight bond strength measurements was 11.0 MPa (s.d.=2.5).

EXAMPLE 6

An aqueous ferric oxalate solution containing a small amount of nitric acid was applied to eight dentin surfaces followed by washing, drying, and the application of the amino acid N-phenylalanine ("NPA" 10% in acetone) followed by the use of acetone to remove excess unbonded NPA amino acid, and subsequent treatment with a 5% acetone solution of PMDM coupling agent, and then Adaptic® composite as described previously. The average bond strength was 16.3 MPa (s.d.=6.4).

Also considered to be within the scope of the present invention is the use of soluble salts containing various elements forming polyvalent cations. These may include; e.g., Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, In, Sn, Sb, Re, Os, Ir, Ce, Sm, Eu, Yb, Pa, and U. One or more cations of these elements may be used (with or without cations of other elements) together with one or more of the dibasic or polybasic carboxylic acids selected from the group including: dihydroxymaleic, diglycollic, oxalacetic, oxalic, malonic, succinic, glutaric, adipic, pimelic, suberic, azelaic, sebacic, malic, ethane-tetracarboxylic, phloinic, chloramalic, itaconic, citraconic, mesaconic, aconitic, citric, tartaric, chlorosuccinic, mesoxalic, tartaric, tricarballylic, acetone dicarboxylic, iso-citric, alpha-ketoglutaric, saccharic, mucic, talo-mucic, trihydroxyglutaric, phospho-glyceric, dimethyl malonic, N-phenyl-glycine-o-carboxylic, 1:2-cyclopropane-dicarboxylic, cyclopropane-1:1:2-tricarboxylic, cyclobutane-1:1-dicarboxylic, cyclobutane-1:2-dicarboxylic, cyclobutane-1:3-dicarboxylic, cyclobutane-1:1:3:3-tetracarboxylic, alpha-truxillic, beta-isotruxillic, 2:3-diphenylbutane-1:1:4:4-tetracarboxylic, cyclopentane-1:1-dicarboxylic, cyclopentane-1:2-dicarboxylic, apocamphoric, camphoric (d, l isomers), 2:5-dimethyl-cyclopentane-1:1-dicarboxylic, alpha, alpha'-di-sec-butyl-glutaric, hexahydro-phthalic, hexahydro-terephthalic, hexahydro-isophthalic, beta-methyl-adipic, isopropyl-succinic, spiroheptane-carboxylic, alpha-tanacetogendicarboxylic, caronic, pinic, norpinic, methyl-succinic, trimethylsuccinic, 1:1-dimethyl-succinic, dehydrocamphoric, homocamphoric, apocam-

phoric, homoapocamphoric, methyl-nor-homocamphoric, iso-fenchocamphoric, alpha-hydroxyiso-fenchocamphoric, alpha, alpha, alpha' alpha'-tetramethyl glutaric, 1:2-dimethyl succinic, 1:1 dimethyl-glutaric, dehydro-mucic (alpha, alpha' furan-dicarboxylic), o-carboxyphenylthioglycollic, furazan-dicarboxylic, 4:5-triazole-dicarboxylic, meconic, 3:4:5:6-pyridazine-tetracarboxylic, uroxanic, 1:3:5-triazine-2:4:6-tricarboxylic, chelidonic, meta-hemipinic, cinchomeronic, alpha-carbo-cinchomeronic, hydrastic, 3:4:5-trimethoxy-1:2-phthalic, trimellitic, isophthalic, terephthalic, phthalic, 4-methoxy-phthalic acid, and lower-molecular-weight polyacrylic acid and copolymers of acrylic and polymerizable carboxylic acids. The foregoing acids are expressly defined for purposes of this invention as "oligocarboxylic acids." Aqueous, or mixed solvent solutions of these are applied to the substrate surface to which bonding is desired.

Water, solvents, or mixtures of water with other solvents are used to prepare solutions of these cations and anions. These cations and anions can be used together as complex mixtures so as to form adequately soluble salt solutions for the first step of the present method. After exposure of the surface to such solutions, for a suitable length of time and at a suitable temperature, the excess solution and soluble reaction products can be washed away with water or the same or a different solvent mixture to obtain the desired structure and chemical composition of an altered surface. Not all combinations of cations and anions may be efficacious (e.g., aqueous solutions of titanium oxalate, titanium fluoride and titanium potassium oxalate yielded poor results when substituted for ferric oxalate), and an oxidizing or reducing agent and/or a photoinitiating agent such as camphoroquinone with an amine or amino acid may be advantageously employed in some cases to facilitate the polymerization of the monomeric components such as PMDM and/or its analogs.

EXAMPLE 7

Two dentin surfaces were treated with an aqueous solution of pH 1.3 (703 mOsm) containing cupric cations and oxydiacetic (diglycollic) acid and sulfate anions; with an acetone solution of NTG-GMA; with an acetone solution of PMDM; then with a UV light. A composite resin bonded to these two surfaces with strengths of 1,480 and 1,920 psi, respectively; the dentin broke cohesively when the latter was tested.

Alternatively, the substrate surface may be acidified or treated with an acidic solution, e.g., with aqueous citric acid, in advance of application of the salt(s).

EXAMPLE 8

Dentin surfaces of 5 extracted teeth were treated with an isotonic citric acid solution; then with an aqueous solution containing cations of iron, copper, manganese, and cobalt, and anions of oxalic, citric, oxydiacetic, and tartaric acids, and ammonium ions. After rinsing with water and drying with an air stream, an acetone solution of NTG-GMA was then applied to the pretreated surfaces followed by an acetone solution of PMDM. A UV light was shined on the surfaces, and mixed composite resin was placed on each in the usual way. After immersion in water for one week the tensile adhesive bond strengths were found to average 2,400 psi. (16.5 MPa). In one of these, which broke at 3,230 psi, a piece of dentin was pulled out of the tooth surface when the bond broke.