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ADHESION PROMOTING DENTAL MATERIALS

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ABSTRACT OF THE DISCLOSURE

Polymerizable liquid condensation products that are also surface-active can be used for dental materials as primers or as monomers to mediate adhesive bonding between particulate fillers and between polymerizing formulations and surfaces such as tooth structure. Preferred the acid-catalyzed condensation products are (I) 2-methacryloxyethyl vanillate, (II) 2 - methacryloxyethyl-p-hydroxybenzoate, and (III) 2-methacryloxyethyl gallate. When surfaces of extracted teeth were wetted with the minimal amount of viscous liquid (I) and a hardening dimethacrylate composite material was applied, the average tensile bond strength was significantly raised (from 18 to 30 kg. f./cm.^{2}).

The mechanism appears to be that the electron-withdrawing effect of the carboxylate group in the aforementioned compounds and in other similar compounds encompassed in the scope of this invention deactivates the phenolic hydroxyl group toward degradative chain transfer with free radicals to the extent that the compounds homopolymerize and copolymerize rapidly when initiated with an amineperoxide system or with other free radical generating initiator systems. In contrast with eugenol, when product (I) containing 0.6% of N,N-dimethyl-symm-xylidine was mixed with zinc oxide powder containing 1.0% benzoyl peroxide, it hardened in about 4 minutes and had an average diametral tensile strength of 154 kg. f./cm.^{2} and an average compressive strength of 1180 kg. f./cm.^{2}.

THE INVENTION

Since the products of this invention have the combined properties of being liquids of moderate viscosity, have the ability to rapidly polymerize, copolymerize or both, forming hard and strong organic polymers, and since they promote a significant increase in adhesion to metal oxide-containing surfaces even after prolonged immersion in water, they provide the ingredients for numerous applications, including the formation of adhesive composite materials, adhesive polymers, and as surface-active coupling agents they mediate bonding between hardening resins and suitable substrates that would otherwise lack adhesion after subjection to the effects of moisture. Specifically, the products of this invention have present utility as polymerizable adhesives, as cavity liners and varnishes and as an ingredient of a composite dental material containing particulate matter.

Presently available adhesion-promoting materials are solids that must be dissolved in inert volatile solvents (such as the surface-active comonomer described in U.S. Pat. 3,200,142 Bowen, which was the reaction product of N-phenyl glycine and a compound selected from glycidyl methacrylate and glycidyl acrylate). Additional prior art provisions are aqueous solutions of polyacrylic acid which harden by reaction with powdered zinc oxide admixed with minor quantities of other materials. This admixture of solution and powder comprising zinc oxide exhibits a degree of adhesiveness to hard tooth tissues and other metal-containing substrates (Smith, D. C. British Dental Journal, vol. 125, p. 381, November 1968). None of the other dental restorative materials have a significant degree of specific chemical adhesion to the hard tooth tissues which have not received special chemical treatments which are themselves responsible for the mediation of adhesive bonding.

Thus, the compounds of the present invention go beyond the materials previously available by having a combination of properties which include fluidity in the absence of solvents or diluents, ability to homopolymerize rapidly, ability to copolymerize with other monomers rapidly (e.g., with methacrylates of a filling), the ability to adhere to the surfaces of admixed particles, fibers, flakes, or other descrete solid materials constituting a discontinuous phase and by virtue of the adhesion-promoting characteristics converting what would otherwise be inert fillers of these types to be reinforcing fillers of this type, and to furthermore adhere either as a neat hardening resin or as a hardening composite resin to surfaces containing various metal oxides, including the calcium of the hard dental tissues of teeth.

Applications of these characteristics include the attachment of orthodontic appliances, fixed prosthetic appliances, temporary as well as relatively permanent restorative materials as restorations in prepared cavities of teeth, and the filling of developmental pits and fissures for the prevention of dental decay.

PRIOR ART

The following patents and literature references are cited generally to show the state of the prior art:

U.S. Pat. 3,200,142 R. L. Bowen; U.S. Pat. 3,066,112 R. L. Bowen; Pat. 3,539,526 Ser. No. 701,539, filed January 30, 1968, R. L. Bowen; Smith, D.C. British Dental Journal, vol. 125, page 381, November 1968; Brauer, G. M., McLaughlin, R., and Huget, E. F. Journal of Dental Research, vol. 47, page 622, July 1968; Peyton, F. A., et al. Restorative Dental Materials, 2d edition, C. V. Mosby Company, St. Louis, 1964, pages 183, 505, and 519; Skinner, E. W., and Phillips, R. W. The Science of Dental Materials. W. B. Saunders Co., Philadelphia, 1967, pages 476–486 and 510–515; Peyton, F. A., et al. Restorative Dental Materials, 3rd edition, C. V. Mosby Co., St. Louis, 1968, pages 183 and 444–450.

SCOPE OF INVENTION

Encompassed by the broad operable coverage of the present invention are also other examples such as the following: the condensation reaction product of 2-hydroxyethyl methacrylate with protochatachuic acid (3,4-dihydroxybenzoic acid), α-resorcylic acid (3,5-dihydroxybenzoic acid), β-resorcylic acid (2,4-dihydroxybenzoic acid, 2,4-dihydroxybenzenecarboxylic acid), gentisic acid (2,5-dihydroxybenzoic acid, 5-hydroxysalcylic acid), salicylic acid (2-hydroxybenzoic acid), and condensation reaction products of the foregoing acids with 2-hydroxy ethylacrylate, and addition reaction products of the foregoing acids wherein the carboxylic group reacts with the epoxy group of glycidyl methacrylate, glycidyl acrylate, or allyl glycidyl ether, and more generally, reaction products of the general formula: