

ADHESION-PROMOTING AGENTS INCORPORATING POLYVALENT CATIONS

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BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to methods of improving adhesive bonding of acrylic and other resins to industrial and dental substrates, and more particularly to dental restoration methods and methods of improving adhesion of composite dental materials to dentin and enamel. More specifically, methods for durable adhesive bonding of composite resins to dentin are disclosed with the objects of improving treatment of cervical erosions, root caries, and other dental conditions and of eliminating much mechanical cutting of dentin now required for retention of restorations.

The complete disclosures of U.S. Pat. Nos. 4,514,527, 4,521,550, 4,588,756 and 4,659,751, and U.S. patent application Ser. No. 07/791,999, filed Nov. 14, 1991 are expressly incorporated herein by reference.

2. Description of the Prior Art

For many years, advances in the study of methods of adhesive bonding of composite materials to hard tooth tissues have evolved by small increments. Previous experiments in adhesive bonding of composite materials to dentin demonstrated beneficial effects from cleansers, mordants, and adhesion promoting coupling agents; see, for example, Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. XXII. The Effects of a Cleanser, Mordant, and PolySAC on Adhesion Between a Composite Resin and Dentin", 59 J. Dent. Res. 809-814 (1980); Bowen, R. L., "Use of Polyfunctional Surface-Active Comonomer and Other Agents to Improve Adhesion Between a Resin or Composite Material and a Substrate", U.S. Pat. No. 4,251,565, February 1981; Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. XIX. Solubility of Dental Smear Layer in Dilute Acid Buffers", 28 Int'l Dent. J. 97-104 (1978); Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. VII. Metal Salts as Mordants for Coupling Agents", in Moskowitz, H.; Ward, G.; & Woolridge, E., (eds.); Dental Adhesive Materials, pp. 205-221, Proceedings from Symposium held Nov. 8-9, 1973 at the Hunter-Bellevue School for Nursing, New York City, Prestige Graphic Services (1974).

The rationale for using a surface-active comonomer as a coupling agent to improve bonding has been supported by previous data. Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. II. Bonding to Dentin Promoted by a Surface-Active Comonomer", 44 J. Dent. Res. 895-902 (1965); Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. III. Bonding to Dentin Improved by Pretreatment and the Use of a Surface-Active Comonomer", 44 J. Dent. Res. 903-905 (1965); Bowen, R. L., "Adhesive Bonding of Various Materials to Hard Tooth Tissues. IV. Bonding to Dentin, Enamel, and Fluorapatite Improved by the Use of a Surface-Active Comonomer", 44 J. Dent. Res. 906-911 (1965); Bowen, R. L., "Adhesive Bonding of Various Materials to Hard

Tooth Tissues V. The Effect of a Surface-Active Comonomer on Adhesion to Diverse Substrates", 44 J. Dent. Res. 1369-1373 (1965). The addition reaction product of N-phenylglycine and glycidyl methacrylate (NPG-GMA) and the addition reaction product of N-phenylglycine and p-chlorophenylglycidyl ether (NPG-CGE) are disclosed, respectively, as vehicles to improve adhesive bonding to a limited extent in Bowen. U.S. Pat. No. 3,200,142, Aug. 10, 1965, and in Bowen, British Pat. No. 1,448,134 and U.S. Pat. No. 3,785,832, Jan. 15, 1974.

Methods for preparing surfaces, such as dentin, enamel, or other natural or industrial substrates, more particularly surfaces containing or capable of binding metallic ions, for adhesion of composite materials or resins have been disclosed in U.S. Pat. Nos. 4,514,527, 4,521,550, 4,588,756 and 4,659,751 to Bowen. These methods include, inter alia, treating such surfaces with acidic aqueous solutions of inorganic acids, polycarboxylic acids, and metal salts of such acids comprised of transition metals capable of changing valence states, washing away the dissolved debris, and then treating the resulting surfaces with adhesion-promoting agents such as N-arylglycine and derivatives, including derivatives having at least one polymerizable moiety, and adhesive bonding monomer agents, such as the reaction products of dianhydrides with molecules containing at least one methacrylate, acrylate or other polymerizable group and also one reactive hydroxyl group, or primary or secondary amino group; 4-methacryloxyethyltrimellitic anhydride and its dicarboxylic acid hydrolysis derivative; and/or other compounds containing at least one group or moiety capable of free radical polymerization and at least one aromatic ring or moiety containing electron-withdrawing substituents that do not interfere with free radical polymerization.

In the prior art, amino acids, including N-arylglycine and derivatives and including derivatives having at least one polymerizable moiety, were in the acidic form (i.e., the carboxyl groups being protonated by the low pH of the solutions) and/or in the form of a monovalent salt of an alkali element, such as sodium or potassium, or as a readily-hydrolyzable lower alkyl or aryl ester (see U.S. Pat. No. 4,659,751, col. 6, line 58). When these amino acids are in the protonated or zwitterionic form, they are subject to undesirable degradation, especially when in solution, between the time of manufacture and utilization. When they are in the form of monovalent alkali metal salts, they cannot provide "molecular ionic bridging" as described hereinbelow. In particular, mixtures of alkali metal salts with protonated or zwitterionic forms of these agents, as described in U.S. Pat. No. 4,964,911, suffer from both of these disadvantages.

Although an acid-etch technique had been effective in beneficiating the bonding of composite and unfilled resins to enamel of teeth, no method had existed until recently for achieving strong adhesive bonding between composite and unfilled resins and dentin to the same useful degree. Many investigators have been attempting to achieve significantly enhanced adhesive bonds to both dentin and enamel and various other substrates for well over twenty-five years with limited success. The present invention represents an improvement in this area of technology.

SUMMARY OF THE INVENTION

It has recently been discovered that the cleansing and "mordanting" procedures used in the prior art to re-