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I, John Gordon Hinde, of Spruson & Ferguson, St Martins Tower, 31 Market Street, Sydney, New South Wales 2000, Australia, being the patent attorney for the Applicant(s)/Nominated Person(s) in respect of Application No 34253/93 state the following:-

The Applicant(s)/Nominated Person(s) has/have entitlement from the actual inventor(s) as follows:-

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DATED this 20th day of June 19 94

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IRN: 275220

INSTR CODE: 58400

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AU9334253

(12) PATENT ABRIDGMENT (11) Document No. AU-B-34253/93
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 680608

- (54) Title
METHOD FOR ADHERING TO HARD TISSUE
- (51)⁵ International Patent Classification(s)
A61K 006/00 A61K 006/08 C09D 129/04 C09D 133/10
A61K 006/083 A61K 006/087 A61K 006/097
- (21) Application No. : 34253/93 (22) Application Date : 30.12.92
- (87) PCT Publication Number : WO93/12760
- (30) Priority Data
- (31) Number (32) Date (33) Country
815404 31.12.91 US UNITED STATES OF AMERICA
- (43) Publication Date : 28.07.93
- (44) Publication Date of Accepted Application : 07.08.97
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- (56) Prior Art Documents
GB 2217989
EP 234934
US 4645456
- (57) Claim

1. A method for adhering to or coating dentin, comprising the steps of:

(a) applying to said dentin adhesively effective amounts of an acid and a water-dispersible film former, wherein said film former comprises

(i) a polymer having a weight average molecular weight of at least 1100 and

(ii) an adhesively effective amount of a polymerizable monomer wherein said acid, being different from said polymer, has a pKa less than or equal to that of phenol; and

(b) hardening said film former to provide adhesive shear strengths of at least 7 MPa to dentin.

24. A method for adhering to or coating dentin, comprising the steps of:

(a) applying to said dentin adhesively effective amounts of a water-dispersible film former comprising:

i) an adhesively effective amount of a polymer containing an acid functionality having a pKa less than or equal to that of phenol and having a weight average molecular weight of at least 1100;

ii) an adhesively effective amount of a polymerizable monomer; and

iii) water; and

(b) hardening said film former by exposing said film former to actinic radiation to provide adhesive shear strengths of at least 7 MPa.

61. A kit for adhering to or coating hard tissue, comprising:

a water dispersible primer comprising adhesively effective amounts of an acid having a pKa less than or equal to that of phenol and a film former comprising a polymer having a weight average molecular weight of at least 1100 and a polymerizable monomer; and

one or more of the dental materials selected from the group consisting of restoratives, adhesives, acid etchants, cements and sealants.

64. A kit for adhering to dentin comprising:

(a) an acid having a pKa less than or equal to that of phenol;

(b) a film former comprising a polymer having a weight average molecular weight of at least 1100 and a polymerizable monomer; and

(c) one or more of the dental materials selected from the group consisting of restoratives, adhesives, cements and sealants.

OPI DATE 28/07/93 APPLN. ID 34253/93
AOJP DATE 30/09/93 PCT NUMBER PCT/US92/11290



AU9334253

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A61K 6/00	A1	(11) International Publication Number: WO 93/12760 (43) International Publication Date: 8 July 1993 (08.07.93)
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(54) Title: METHOD FOR ADHERING TO HARD TISSUE (57) Abstract The invention provides a pretreatment method and primer that is applied directly to the hard tissue. The invention has particular utility for adhering to or coating sclerotic dentin and cervical enamel or for adhering to or coating hard tissue in a high humidity environment. The primer enables formation of extremely strong bonds to dentin. The method comprises the steps of: (a) applying to the hard tissue adhesively effective amounts of an acid and a waterdispersible film former comprising a polymer and (b) hardening the film former. Primer compositions are provided for use in this method, comprising a mixture of an acid and a film former comprising a polymer prior to hardening, the mixture being in the form of a film atop the hard tissue.		

METHOD FOR ADHERING TO HARD TISSUE

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Technical Field

This invention relates to a method for adhering to hard tissue. This invention also relates to adhesive compositions for use on hard tissue.

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Background Art

In recent years there has been intense interest in the dental field in adhesives that bond to hard tissues such as dentin. Forces generated by the polymerization contraction of dental restorative materials suggest that a minimum adhesion strength for bonding restorative materials to hard surfaces in in vivo clinical procedures would be desirable. For example, M. Jensen, *Polymerization Shrinkage and Microleakage International Symposium on Posterior Composite Resin Dental Restorative Materials*, 243-44 (1985) reports a contraction force of 7.3 MPa. for conventional composite materials. In many instances the minimum adhesive strength has not been achieved, resulting in direct communication between dentin and the oral cavity via gaps between the dental restorative material and the cavity walls. This may be responsible, in part, for patient complaints of sensitivity and for pulpal irritation and inflammation. See, Tao, *The relationship between dentin bond strengths and dentin permeability Dental Materials*, Vol. 5, 133-39 (1989).

25 Recently a novel priming method was developed in the laboratory of the assignee of this invention and is sold commercially as ScotchBond 2™ Light Cure Dental Adhesive with Scotchprep™ Dentin Primer (commercially available from 3M). This priming method has achieved average shear strengths in vitro in excess of 20 MPa. U.S. Patent No. 4,719,149 (Aasen et al.) describes that invention as an acid and a water-soluble film former useful for priming hard tissue (e.g., dentin). The acid has a pKa less than or equal to that of phenol. The calcium salt(s) of the acid are soluble in the film former. The film former is exemplified as comprising various difunctional and monofunctional monomers and optional cosolvents with 2-hydroxyethylmethacrylate and water being preferred.

30 Kusumoto et al., U.S. Patent No. 4,535,102 discloses an adhesive coating material for a hard tissue comprising (1) a polymer having an acid value of 30 to 700 and

including in recurring units a hydrophobic group and two carboxyl groups or one carboxylic anhydride group bonded to the polymer, and (2) a polymerizable vinyl compound or a mixture of said polymerizable vinyl compound and an organic titanate compound.

5 Engelbrecht et al., U.S. Patent No. 4,806,381 discloses oligomeric or prepolymeric organic compounds that contain both polymerizable unsaturated groups and acid radicals, their salts or their reactive-derivative radicals. The compounds adhere to biological substrates such as tooth tissue.

10 Beech et al., U.S. Patent No. 4,732,943 discloses an adhesive comprising (a) a condensate of ϵ -caprolactone with one or more acrylic monomers containing hydroxy groups and (b) a polymer containing binding groups capable of binding to the dentin.

One major limitation in the prior art has been the difficulty of adhering to hard tissue which is not dry. This necessitates maintaining a dry tooth surface during the priming procedure which is in practice difficult to ensure. For instance, the oral cavity is
15 inherently humid and the hard tissue is susceptible to fluid perfusion from the pulp chamber. The susceptibility of the tooth surface to this fluid perfusion is believed to be a function of the proximity of the prepared surface to the pulp chamber. Near the pulp, the tubules are very close together and the water content of this deep dentin is very high. See,
20 Pashley, *Dentin: A Dynamic Substrate* Scanning Microscopy, Vol. 3, No. 1, 161-76 (1989).

Additionally, dental materials adhere poorly to sclerotic dentin and cervical enamel. Sclerotic dentin is characterized as hypermineralized dentin (i.e., the dentinal tubular contents are mineralized) and has a coloration that can range from transparent to intense
25 yellow or yellow-brown.

Summary of the Invention

The invention provides a pretreatment (a primer) that is applied directly to the hard tissue. The invention has particular utility for adhering to or coating sclerotic dentin and
30 cervical enamel or for adhering to or coating hard tissue in a high humidity environment. The primer enables formation of extremely strong bonds to dentin (including sclerotic dentin), exhibiting shear strengths as high as 30 MPa., when tested in shear using the procedure described herein. Tests to date indicate that an extremely durable adhesive bond with little or no detectable microleakage can be obtained. The primers of the invention can,
35 if desired, be water-based, thus substantially reducing the need to apply them in a dry

field. The primers of the invention work very well in high humidity environments or when bonding to sclerotic dentin.

The present invention provides, in a first aspect, a method for adhering to or coating dentin, comprising the steps of:

- 5 (a) applying to said dentin adhesively effective amounts of an acid and a water-dispersible film former, wherein said film former comprises
 - (i) a polymer having a weight average molecular weight of at least 1100 and
 - (ii) an adhesively effective amount of a polymerizable monomer wherein said acid, being different from said polymer, has a pKa less than or equal to that of
 10 phenol; and
- (b) hardening said film former to provide adhesive shear strengths of at least 7 MPa to dentin.

For purposes of this invention "hardening" is defined as the formation of a covalently or ionically crosslinked polymer as opposed to merely drying a previously
 15 prepared polymer of its carrier solvent or merely cooling a previously melted thermoplastic polymer.

In a second aspect, the present invention provides a method for adhering to or coating dentin, comprising the steps of:

- 20 (a) applying to said dentin adhesively effective amounts of a water-dispersible film former comprising:
 - i) an adhesively effective amount of a polymer containing an acid functionality having a pKa less than or equal to that of phenol and having a weight average molecular weight of at least 1100;
 - ii) an adhesively effective amount of a polymerizable monomer; and
 - 25 iii) water; and
- (b) hardening said film former by exposing said film former to actinic radiation to provide adhesive shear strengths of at least 7 MPa.

In a third aspect, the present invention provides a method for adhering to or coating dentin, comprising the steps of:

- 30 (a) applying to said dentin adhesively effective amounts of a water-dispersible film former comprising:
 - i) an adhesively effective amount of a polymer containing an acid functionality having a pKa less than or equal to that of phenol and having a weight average molecular weight of at least 1100;
 - 35 ii) an adhesively effective amount of a polymerizable monomer; and
 - iii) water; and
- (b) hardening said film former by exposing said film former to actinic radiation wherein said application occurs in a high humidity environment and provides an adhesive shear strength of at least 5 MPa.

In a fourth aspect, the present invention provides a method for adhering to or coating hard tissue, comprising the steps of:

(a) applying to said hard tissue adhesively effective amounts of a water-dispersible film former comprising:

- 5 i) a polymer containing an acid functionality having a pKa less than or equal to that of phenol and having a weight average molecular weight of at least 1100;
- ii) a polymerizable monomer; and
- iii) water; and

(b) hardening said film former by exposing said film former to actinic radiation,
10 wherein said application occurs in a high humidity environment and provides an adhesive shear strength of at least 5 MPa.

In a fifth aspect, the present invention provides a method for adhering to or coating hard tissue, comprising the steps of:

(a) applying to said hard tissue adhesively effective amounts of an inorganic or
15 organic acid and a water-dispersible film former, wherein said film former comprises:

- (i) an adhesively effective amount of a polymer comprising a carboxylic acid functionality, and having a weight average molecular weight of at least 1100; and
- (ii) an adhesively effective amount of a polymerizable monomer comprising an acrylate or methacrylate functionality;

20 wherein said acid, being different from said film former, has a pKa less than or equal to that of phenol; and

(b) hardening said film former to provide adhesive shear strengths of at least 7 MPa.

In a sixth aspect, the present invention provides a method for adhering to or coating
25 hard tissue, comprising the steps of:

(a) applying to said hard tissue adhesively effective amounts of an inorganic or organic acid and a water-dispersible film former, wherein said film former comprises

(i) an adhesively effective amount of a polymer comprising a polymerizable group selected from the group consisting of acrylates, methacrylates and combinations
30 thereof, and having a weight average molecular weight of at least 1100; and

(ii) an adhesively effective amount of a polymerizable monomer comprising an acrylate or methacrylate functionality;

wherein said acid, being different from said film former, has a pKa less than or equal to that of phenol; and

35 (b) hardening said film former to provide adhesive shear strengths of at least 7 MPa.

In a seventh aspect, the present invention provides a method for adhering an orthodontic bracket to enamel, comprising the steps of:

(a) applying to said enamel adhesively effective amounts of an acid and a water-
40 dispersible film former, wherein said film former comprises

(i) an adhesively effective amount of a polymer having a weight average molecular weight of at least 1100 and

(ii) an adhesively effective amount of a polymerizable monomer, and wherein said acid, being different from said polymer, has a pKa less than or equal to that of phenol;

(b) hardening said film former; and

(c) adhering an orthodontic bracket to said enamel having film former applied thereto.

The present invention also provides novel primer compositions for use in such method, comprising a mixture of an acid and a film former comprising a polymer prior to the hardening step, said mixture being in the form of a film atop said hard tissue.

Thus, in a eighth aspect, the present invention provides a hardenable primer film, said film forming a layer with dentin whose surface has been modified by treatment with an acid having a pKa less than or equal to that of phenol, wherein prior to being hardened said film comprises adhesively effective amounts of a water-dispersible film former comprising:

(i) a polymer having a weight average molecular weight of at least 1100, and

(ii) a polymerizable monomer, said film being capable of providing an adhesive shear strength of at least 7 MPa.

In a ninth aspect, the present invention provides a hardenable primer film, said film forming a layer with dentin whose surface has been modified by treatment with an acid having a pKa less than or equal to that of phenol, wherein prior to being hardened said film comprises adhesively effective amounts of a water-dispersible film former comprising:

(i) a polymer having a weight average molecular weight of at least 1100, and

(ii) a polymerizable monomer, wherein said film is capable of providing an adhesive shear strength when applied in a high humidity environment of at least 5 MPa.

In a tenth aspect, the present invention provides kit for adhering to or coating hard tissue, comprising:

a water dispersible primer comprising adhesively effective amounts of an acid having a pKa less than or equal to that of phenol and a film former comprising a polymer having a weight average molecular weight of at least 1100 and a polymerizable monomer; and

one or more of the dental materials selected from the group consisting of restoratives, adhesives, acid etchants, cements and sealants.

In an eleventh aspect, the present invention provides a kit for adhering to or coating hard tissue, comprising:

a water dispersible primer comprising adhesively effective amounts of a film former comprising (i) a polymer containing an acid functionality having a pKa less than or equal to that of phenol and having a weight average molecular weight of at least 1100 and (ii) a polymerizable monomer; and

- 5 one or more of the dental materials selected from the group consisting of restoratives, adhesives, acid etchants, cements and sealants.

In a twelfth aspect, the present invention provides a kit for adhering to or coating hard tissue, comprising:

- a water dispersible primer comprising adhesively effective amounts of an acid
10 having a pKa less than or equal to that of phenol and a film former comprising a polymer having a weight average molecular weight of at least 1100 and a polymerizable monomer; and

one or more of the dental materials selected from the group consisting of restoratives, adhesives, acid etchants, cements and sealants.

- 15 In a thirteenth aspect, the present invention provides a kit for adhering to dentin comprising:

- (a) an acid having a pKa less than or equal to that of phenol;
(b) a film former comprising a polymer having a weight average molecular weight of at least 1100 and a polymerizable monomer; and
20 (c) one or more of the dental materials selected from the group consisting of restoratives, adhesives, cements and sealants.

Detailed Description

In the practice of the present invention, the hard tissues which can be adhered to or coated include human and animal tissues such as teeth (including the component parts
25 which are enamel, dentin, and cementum), bone, fingernails, and hoofs. The invention has particular utility for adhering to or coating dentin, sclerotic dentin, enamel, and cervical enamel.

The acid and film former can be applied to hard tissue concurrently or sequentially. If they are applied sequentially, then if desired the acid can be rinsed from the hard tissue
30 (e.g., using a water rinse) before application of the film former, or the film former can be applied to the acid without an intermediate rinsing step. For brevity, formulations comprising the film former will sometimes be referred to as the "primer", regardless of whether the concurrent or sequential application method is employed. Thus, when the acid and film former are applied to the hard tissue concurrently, then the acid and film
35 former will sometimes be referred to collectively as the "primer". When the acid and film former are applied to the hard tissue sequentially, then the acid, if in a solvent, will sometimes be referred to as an "etchant" and the film former will sometimes be referred to as the "primer".

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In one method of the invention, the primer is permitted to stand on the hard tissue for a desired period of time, readily volatile cosolvents are removed therefrom (e.g., by air-

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drying) to modify the surface of the hard tissue and leave a residual film on the surface of the hard tissue (and in the case of dentin to form a "hybrid layer" with the hard tissue), the residual film is overcoated with a layer of additional film former (the additional film former can be water-soluble or water-insoluble but should preferably form a
5 homogeneous solution when combined with the residual film), then the additional film former and residual film are hardened and optionally overcoated with a composite, restorative, glass ionomer cement, sealant or other hardenable coating (hereafter such composites, restoratives, glass ionomer cements, sealants, and other hardenable coatings will be referred to collectively as "restoratives"). As used herein, "surface modified hard
10 tissue" refers to hard tissue that has been exposed to the primers of the invention. As used herein, "hybrid layer" refers to the layer of resin-reinforced dentin that consists of collagen and perhaps hydroxyapatite that is infiltrated and surrounded by the monomers, oligomers and polymers of the film former and the optional additional film former. Thus the invention enables priming of hard tissue in order to improve the bond strength or
15 durability of a restorative or coating applied thereto.

Acids for use in the present invention can be inorganic or organic acids, and if organic can be monomeric, oligomeric or polymeric. If desired, a precursor to the acid such as an acid anhydride, e.g., 4-Methacryloxyethyl Trimellitate Anhydride (4-META),
20 acid halide (including inorganic acid halides such as Lewis acids, e.g., ferric chloride, and organic acid halides), or ester can be used in place of the acid itself, e.g., to generate the desired acid in situ. Suitable acids include mineral acids, carboxylic acids, sulfonic acids, and phenols, with carboxylic acids, alkylsulfonic acids, arylsulfonic acids, and phosphonic acids being preferred.

25 The acid has a pKa in water that is less than or equal to that of phenol. Preferably, the pKa of the acid is between about -20 and about +10, more preferably between about -10 and about +5.

The acid, when applied concurrently with the film former, should be sufficiently soluble in the film former and in a sufficient amount (including any optional cosolvents
30 that are present in the film former) to provide the desired degree of adhesion for the particular hard tissue and application involved. For example, on dentin the degree of adhesion preferably is sufficient to provide an average measured shear strength of at least 7 MPa., and more preferably at least 12 MPa. Preferably, on dentin the degree of adhesion is sufficient to provide an average measured shear strength in a humid
35 environment (i.e., as tested in a room temperature humidity chamber with a relative

humidity greater than about 90%) of at least 5 MPa., more preferably at least 7 MPa., and most preferably at least 12 MPa.

Preferably, the calcium salt of the acid is also soluble in the film former (including any optional cosolvents that are present in the film former) or in the etchant solution (e.g.,
5 when the acid is applied sequentially with the film former). Acids having insoluble calcium salts may also be used in the primers of the present invention. For example, when the acid and film former are applied sequentially the acid may form insoluble calcium salt(s) that are insoluble in: the optional cosolvent; the subsequently applied film former (including any optional cosolvents that are present in the film former); or both. However,
10 these salt(s) can be rinsed from the hard tissue, prior to application of the film former, to thereby not detrimentally affect the adhesion.

A "soluble" acid or calcium salt of an acid, as used herein, is an acid or salt that when mixed with the film former (including any optional cosolvents that are present in the
15 film former) under the desired conditions of use dissolves to form a homogeneous liquid mixture. Such conditions of use include temperature (e.g., body temperature), time (e.g., "standing time", that is, the amount of time the primer is allowed to remain on the surface of the hard tissue before hardening of the film former), and concentration (e.g., the concentration of acid and of calcium salt that may be formed in the film former when
20 primer is applied to calcium-containing hard tissue such as teeth or bones). Alternatively, when the acid and film former are applied sequentially a "soluble" acid or calcium salt of an acid, as used herein, is an acid or salt that when mixed with an optional cosolvent under the desired conditions of use dissolves to form a homogeneous liquid mixture.

The acid can be liquid or a solid; if a solid it should be dissolved in a suitable
25 solvent to enable the acid to wet the hard tissue. Liquid acids can also be dissolved in a suitable solvent, e.g., in order to facilitate wetting. Preferred solvents for the acid are the film former cosolvents discussed in more detail below.

Suitable inorganic acids include HBr, HCl, and HNO₃. Suitable organic acids include acetic acid, α-chloropropionic acid, 2-acrylamido-2-methylpropane sulfonic acid,
30 acrylic acid, benzenesulfonic acid, benzoic acid, bromoacetic acid, 10-camphorquinone-sulfonic acid, 10-camphorsulfonic acid, chloroacetic acid, citraconic acid, citric acid, dibromoacetic acid, dichloroacetic acid, di-Hema ester of 1,2,4,5 benzenetetracarboxylic acid, 2,4-dinitrophenol, formic acid, fumaric acid, 2-hydroxy-4-methoxybenzophenone-5-sulfonic acid, maleic acid, methacrylic acid, 2-naphthalene sulfonic acid, nitric acid, oxalic
35 acid, p-nitrophenol, phenol, phosphoric acid, phosphorous acid esters (such as 2,2'-bis(a-

methacryloxy-b-hydroxypropoxyphenyl) propane diphosphonate (Bis-GMA diphosphonate), dibutyl phosphite, di-2-ethyl-hexyl phosphate, di-2-ethyl-hexyl phosphite, hydroxyethyl methacrylate monophosphate, glyceryl dimethacrylate phosphate, glyceryl-2-phosphate, glycerylphosphoric acid, methacryloxyethyl phosphate, pentaerythritol triacrylate monophosphate, pentaerythritol trimethacrylate monophosphate, dipentaerythritol pentaacrylate monophosphate, and dipentaerythritol pentamethacrylate monophosphate), pivalic acid, propionic acid, sulfuric acid, toluene sulfonic acid, tribromoacetic acid, trichloroacetic acid, trifluoroacetic acid, trifluoromethanesulfonic acid, and trihydroxybenzoic acid. Mixtures of such acids can be used if desired.

When the acid and film former are applied concurrently, then a preferred amount of acid to be dissolved in the film former will be between about 0.001M and the limit of solubility. The optimum amount depends in part on the pKa of the acid. For example, for sulfonic acids, concentrations between about 0.01M and about 0.5M are preferred. When the acid and film former are applied sequentially, then a preferred amount of acid to be dissolved in the cosolvent will be between about 0.001M and the limit of solubility. The optimum amount depends in part on the pKa of the acid.

The film former is a water-dispersible substance or water-dispersible mixture of substances, such substance(s) being organic monomers, oligomers, polymers, or cosolvents, wherein the film former contains at least one polymer prior to the hardening step, and is capable of forming a hardenable (e.g., polymerizable) continuous or semicontinuous film on the surface of the hard tissue. As used herein, a "water-dispersible" film former has a water dispersibility or more preferably a water solubility (exclusive of any water that may be present in the film former) of at least about 5 weight percent. Most preferably, the film former can be mixed with water in all proportions. For brevity, dispersible and soluble will sometimes be referred to collectively as dispersible. As used herein, "solubility" means the capability of a substance to form a solution, i.e., either a true solution or a colloidal solution. A true solution being a uniformly dispersed mixture at the molecular or ionic level, of one or more substances (the solute) in one or more substances (the solvent). These two parts of a solution are called phases. A colloidal dispersion is often called a solution. Since colloidal particles are larger than molecules it is strictly incorrect to call such dispersions solutions; however this term is widely used in the literature. As used herein, "dispersibility" means the capability of a substance to form a dispersion, i.e., a two-phase system where one phase consists of finely divided particles (often in the colloidal size range) distributed throughout a bulk substance, the particles being the disperse or internal phase and the bulk substance the continuous or external

phase.

Preferred film formers contain one or more substances having a sufficient number of water-dispersing groups such as hydroxyl groups, carboxyl groups, sulfonic acid groups, cationic salts (e.g., ammonium, phosphonium or sulfonium groups), amide linkages or polyether linkages to render the film former water-dispersible. The film former, prior to removal of any volatile components, preferably wets the hard tissue and most preferably has a sufficiently low viscosity to enable it to flow into interstices that already exist in the surface of the tissue or that are created therein by the action of the acid. After removal of any volatile components the film former preferably has a sufficiently high viscosity to enable it to resist displacement by dentinal fluids or other extraneous liquids. To assist in hardening the film former, it preferably contains one or more polymerizable substances. Addition polymerizable substances (e.g., vinyl compounds such as acrylates and methacrylates) are especially preferred. The film former can also contain appropriate polymerization catalysts (e.g., photoinitiators) to assist in hardening the film former.

Suitable polymer components in the film former include linear, branched or cyclic polymers formed prior to the hardening step. For purposes of this invention, a polymer is a chemical compound having at least two repeat units. They can be polymers of ethylenically unsaturated monomers or they can be polymeric compounds like polyester, polyamide, polyether, polyethyleneglycol, polyethyleneglycol dimethacrylate and diacrylate, polysaccharide, cellulosic, polypropylene, polyacrylonitrile, polyurethane, poly(vinyl chloride), poly(methyl methacrylate), phenol-formaldehyde, melamine-formaldehyde, and urea-formaldehyde. Mixtures of such polymers can be used if desired.

Preferred polymers are the polymers of ethylenically unsaturated monomers. These polymers may be homo- or co-polymers and may contain hydrophilic or hydrophobic groups. The polymer may optionally contain acid groups, their salts, or their reactive derivative groups. Particularly preferred polymers contain reactive groups that further react (i.e., crosslink or copolymerize) with the other components of the film former, the overcoat resin (i.e., the additional film former), or the dental restorative. Addition polymerizable reactive groups (e.g., vinyl groups such as acrylates and methacrylates) are especially preferred. Polymers of ethylenically unsaturated monomers are often used in dental glass ionomer cements. These polymers are especially useful in the present invention as they generally have good biocompatibility, are dispersible in water and have a suitable molecular weight. Particularly preferred polymers contain functional groups that

have an affinity for the hard tissue. For example, such groups include β -dicarbonyl groups and carboxylic acid groups. The polymer component of an ionomer cement is often a copolymer of acrylic acid and itaconic acid, although other monomers may be incorporated, and are herein referred to as polyalkenoic acids. See generally, Prosser et al.,
5 Developments in Ionic Polymers - 1, Chapter 5, Applied Science Publishers (London and New York, 1983). Recently such polymers have been further modified in the laboratory of the assignee of this invention by the incorporation of addition polymerizable reactive groups as mentioned above. Their preparation is described in European Patent Application No. 0 323 120 and in U.S. Patent No. 5,130,347.

10 Suitable polymeric compounds of the invention have a weight average molecular weight prior to hardening of more than about 500, although preferably no greater than 2,000,000. More preferably, polymeric compounds of the invention have a weight average molecular weight prior to hardening of between about 1,000 and 1,000,000 evaluated
15 against a polystyrene standard using gel permeation chromatography. Most preferably, polymeric compounds of the invention have a weight average molecular weight prior to hardening of between about 5,000 and 200,000.

Suitable monomer components in the film former include 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate ("HEMA"), 2- and 3-hydroxypropylacrylate and
20 methacrylate, 1,3- and 2,3-dihydroxypropylacrylate and methacrylate, 2-hydroxypropyl-1,3-diacrylate and dimethacrylate, 3-hydroxypropyl-1,2-diacrylate and dimethylacrylate, pentaerythritol diacrylate and dimethacrylate, acrylic acid, methacrylic acid, 2-trimethylammonium ethylmethacrylic chloride, 2-acrylamido-2-methylpropane-sulfonic acid, acrylamide, methacrylamide, 2-hydroxyethylacrylamide and methacrylamide, N,N-
25 bis(2-hydroxyethyl)acrylamide and methacrylamide, N-alkyl-N-hydroxyethyl acrylamides and methacrylamides, 2- and 3-hydroxypropylacrylamide and methacrylamide, methacrylamidopropyltrimethylammonium chloride, polyethyleneglycol (400) diacrylate and dimethacrylate, glycerol dimethacrylate and diacrylate, glycerol monomethacrylate and monoacrylate, pentaerythritol trimethacrylate and triacrylate, and mixtures thereof. It is
30 expected that where an acrylate monomer is suitable the methacrylate analog will likewise be suitable.

The film former preferably comprises one or more suitable cosolvents. The cosolvent(s) aid in wetting the hard tissue and in solubilizing or dispersing the substances. Suitable cosolvents include water, alcohols such as methanol, ethanol, 1-propanol, 2-
35 propanol, and 2-methyl-2-propanol, ketones such as acetone and methyl ethyl ketone,

aldehydes such as formaldehyde, acetaldehyde, propionaldehyde, acrolein, glutaraldehyde and 2-hydroxy-adipaldehyde, amides such as acetamide and N,N-dimethylformamide, and other substances such as tetrahydrofuran and dimethyl sulfoxide. The film former preferably contains less than about 95 weight percent cosolvent, more preferably between
5 about 15 and about 85 weight percent cosolvent.

The primer may contain only acid and film former. Other adjuvants such as polymerization catalysts, medicaments, fluoride compounds, indicators, dyes, wetting agents, buffering agents, thixotropes and the like can be included in the primer, contingent upon attainment of the desired degree of bonding performance and suitability for use on
10 the desired hard tissue.

Hard tissue to which the primer is applied preferably is first cleaned using conventional methods (e.g., by abrading it with a bur), rinsed (e.g., using water) and dried (e.g., using air). If desired, deep excavations in teeth can be lined with a conventional
15 basing material, (e.g., calcium hydroxide or a glass ionomer cement).

The acid and film former should be allowed to stand on the surface of the hard tissue long enough to provide the desired degree of priming. The standing time will depend upon the particular acid and film former employed, whether a concurrent or sequential application of acid and film former is employed, the type of hard tissue and its
20 intended use, and the time available for carrying out the priming procedure. For priming dentin and enamel, standing times less than about 5 minutes, and preferably about 5 seconds to one minute provide very effective priming, although shorter or longer times can be used if desired.

As mentioned above, the primer preferably is overcoated with an optional layer of
25 additional water-dispersible or water-indispersible film former, and then hardened. Preferably, such additional film former is copolymerizable with the residual film formed by removal of volatile cosolvents from the primer, and contains a polymerization catalyst (preferably a photoinitiator) capable of hardening the residual film and additional film former. If desired, the additional film former can contain conventional fillers, and can also
30 contain adjuvants of the type described above. A particularly preferred additional film former is obtained by combining (1) the dimethacrylate ("Bis-GMA") derived from the reaction between methacrylic acid and the diglycidyl ether of bisphenol A with (2) a hydrophilic monomer such as HEMA, hydroxypropyl methacrylate, or methacrylic acid. Suitable monomers for use in the additional film former include the monomers described
35 above as well as tetrahydrofurfural methacrylate, glyceryl-1,3-dimethacrylate,

triethyleneglycol dimethacrylate, ethyl methacrylate, n-hexyl methacrylate, polyethyleneglycol dimethacrylate ("PEGDMA"), and 1,6-hexanediol dimethacrylate. Optionally, the additional film former may contain polymers of the type described above. The additional film former can also contain cosolvents of the type described above.

5 Polymerization catalysts that can be included in the primer or in the additional film former are autocure or light cure catalysts (i.e., catalysts which are sensitive to actinic radiation such as visible light) such as those mentioned in columns 28 and 29 of U.S. Pat. No. 4,539,382, chromophore-substituted halomethyl-s-triazines such as those shown in U.S. Pat. No. 3,954,475, chromophore-substituted halomethyl-oxadiazoles such as those
10 shown in U.S. Pat. No. 4,212,970, and arylodonium salts such as those shown in European Patent Application 0 290 133.

As also mentioned above, the primer and optional additional film former preferably are overcoated with a conventional restorative or coating. The hard tissue can then be
15 finished using conventional techniques. For example, on tooth tissue, the primer can be overcoated with a dental adhesive, dental ionomer cement and/or a dental restorative and used, for example, to restore teeth, to install crowns, bridgework or other prosthetic devices, to bond orthodontic brackets to enamel, to seal pits and fissures or to veneer dentin, cementum or enamel. On bone and hoofs, the primer can be used in conjunction
20 with a conventional filled or unfilled bone cement (e.g., a methyl methacrylate-based cement) to repair fractures or to fill defects. On fingernails, the primer can be used in conjunction with a conventional polymerizable fingernail coating to strengthen a fingernail, alter its shape, color or smoothness or fasten an artificial fingernail thereto.

The adhesive compositions of the present invention are particularly well suited for
25 use in the high humidity environment of the mouth. Humidity values encountered in the mouth may fluctuate widely, depending on such factors as respiratory exhalation, fluid perfusion through the dentinal tubules and lack of control of extraneous fluids by the dental practitioner. When any of the above factors are present the hard tissue may be considered to be in a high humidity environment. Surprisingly, high adhesive shear
30 strengths of restoratives on dental hard tissues may be achieved without the need to take extraordinary steps to protect the tissue from exposure to high humidity. For purposes of in-vitro comparisons, bond strength tests should preferably be compared in a room temperature high humidity chamber with a relative humidity greater than about 90%.

35

Adhesive Strength Test Method

Adhesion to dentin or enamel of the primers of the invention was evaluated as follows:

First, teeth (usually five bovine teeth unless otherwise noted) of similar age and appearance were partially embedded in circular acrylic discs. The exposed portion of each tooth was ground flat and parallel to the acrylic disc using Grade 120 silicon carbide paper-backed abrasive mounted on a lapidary wheel, in order to expose the dentin or enamel. During this and subsequent grinding and polishing steps, the teeth were continuously rinsed with water. Further grinding and polishing of the teeth was carried out by mounting Grade 320 silicon carbide paper-backed abrasive and then Grade 600 silicon carbide paper-backed abrasive on the lapidary wheel. The polished teeth were stored in distilled water, and used for testing within 2 hours after polishing. The polished teeth were removed from the water and dried using a stream of compressed air.

Primer compositions were next applied to the prepared tooth surfaces as described in one of the following procedures:

Application Procedure I - A single drop of primer composition (containing varying amounts of acid and film former) was painted onto each of the polished tooth surfaces with a brush and allowed to stand for 30 to 60 seconds. The primer was then blown dry with compressed air and cured using a 20-second irradiation with a "Visilux™ 2" dental curing light (commercially available from 3M).

Application Procedure II - A single drop of primer composition (containing varying amounts of acid and film former) was painted onto each of the polished tooth surfaces with a brush, allowed to stand for 30 to 60 seconds, and then blown dry with compressed air. An overcoat of additional water-dispersible or water-indispersible film former was applied, gently air thinned and cured using a 20-second irradiation with a Visilux 2 dental curing light.

Application Procedure III - An etchant was painted onto each of the polished tooth surfaces with a brush, allowed to stand for 15 seconds, and then blown dry with compressed air. A single drop of primer composition (containing varying amounts of acid and film former) was painted onto each of the polished tooth surfaces with a brush and immediately blown dry with compressed air. A thin layer of overcoat of additional water-dispersible or water-indispersible film former was painted onto each of the tooth surfaces, gently air thinned and cured using a 10-second irradiation with a Visilux 2 dental curing light.

Application Procedure IV - An etchant was painted onto each of the polished

tooth surfaces with a brush, allowed to stand for 15 seconds (unless otherwise noted), rinsed with distilled water and then blown dry with compressed air. A single drop of primer composition (containing varying amounts of acid and film former) was painted onto each of the polished tooth surfaces with a brush and immediately blown dry with compressed air. A thin overcoat of additional water-dispersible or water-indispersible film former was painted onto each of the tooth surfaces, gently air thinned and cured using a 10-second irradiation with a Visilux 2 dental curing light.

Application Procedure V - In a high humidity chamber (having a temperature of 25 °C and a relative humidity greater than 90%) an etchant was painted onto each of the polished tooth surfaces with a brush, allowed to stand for 15 seconds (unless otherwise noted), rinsed with distilled water and then blown with compressed air. A single drop of primer composition (containing varying amounts of acid and film former) was painted onto each of the polished tooth surfaces with a brush and immediately blown with compressed air. A thin overcoat of additional water-dispersible or water-indispersible film former was painted onto each of the tooth surfaces, gently air thinned and cured using a 10-second irradiation with a Visilux 2 dental curing light.

Previously prepared molds made from a 2-mm thick "Teflon" sheet with a 4 mm diameter hole through the sheet were clamped to each prepared tooth so that the central axis of the hole in the mold was normal to the tooth surface. The hole in each mold was filled with a visible light-curable dental restorative (typically "P-50™" brand universal shade restorative, available from 3M) and cured using a 20-second irradiation. It is believed that the choice of restorative might affect the bond strength values obtained for a given adhesive system. For example, some adhesive systems of the present invention provide very strong bonds to hard tissue that are believed to fail at the restorative-adhesive interface or within the restorative and not at the adhesive-hard tissue interface. A higher strength restorative may increase the measured bond strength for these adhesive systems. Therefore, comparisons between different adhesive systems should be made, wherever possible, using similar restorative systems. The teeth and molds were allowed to stand for about 5 minutes at room temperature, then stored in distilled water at 37 °C for 24 hours unless otherwise noted. The molds were then carefully removed from the teeth, leaving a molded button of restorative attached to each tooth.

Adhesive strength was evaluated by mounting the acrylic disk in a holder clamped in the jaws of an "Instron" apparatus with the polished tooth surface oriented parallel to the direction of pull. A loop of orthodontic wire (0.44 mm diameter) was placed around the restorative button adjacent to the polished tooth surface. The ends of the orthodontic wire

were clamped in the pulling jaw of the Instron apparatus, thereby placing the bond in shear stress. The bond was stressed until it (or the dentin or button) failed, using a crosshead speed of 2 mm/min.

The following examples are offered to aid in understanding of the present invention and are not to be construed as limiting the scope thereof. Unless otherwise indicated, all parts and percentages are by weight.

Example 1

Using the adhesive strength test method outlined above and Application Procedure I, the average shear strength on dentin and enamel of several primer compositions was evaluated. The primers were made from aqueous solutions of various polymers, monomers and optionally maleic acid as listed in Table 1. Set out below in Table I are the run number, ingredients, and average shear strength on enamel or dentin (in MPa.). The sample size (n) for each run in this and the following examples was five unless otherwise noted.

Table 1

Ingredients	Run #	1	2	3	4	5	6 ⁷	7 ⁸
(parts)								
VBP ¹		4.23	1.52	-	10.0	15.0	30.0	10.0
VBP-T ²		-	-	0.76	-	-	-	-
HEMA		2.29	2.02	1.45	40.0	29.0	28.0	36.0
PEGDMA		5.0	-	-	-	-	-	-
Water		3.43	6.43	2.80	50.0	56.0	42.0	54.0
MOST ³		0.075	-	-	-	-	-	-
CPQ ⁹		0.050	0.026	-	0.2	-	0.5	-
Maleic Acid		-	0.52	0.25	4.0	5.0	-	-
DPICl ¹⁰		-	-	-	-	-	3.2	-
<u>Adhesion (MPa.) at 24 hrs.</u>								
Enamel		-	-	12.8	-	9.8	-	-
Dentin		12.1 ⁴	12.5 ⁵	7.7	14.6	6.4	13.8	10.6
<u>Adhesion (MPa.) immediate</u>								
Dentin		-	-	-	-	11.0 ⁶	-	-

1 ("VBP") = the precipitated dry polymer of EXAMPLE 11 of European Published Pat. Application No. 0 323 120.

2 ("VBP-T") = the reaction product of VBP, "MOSTOL" (2,4-Bis-(trichloromethyl)-6-(2-hydroxyethoxy)styryl-s-triazine), and "TMDI" (Tetramethylene diisocyanate). The
5 preparation of this polymer is described in EXAMPLE 2 below and contains in this example approximately 4% triazine functionality by weight.

3 ("MOST") = 2,4-Bis-(trichloromethyl)-6-methoxystyryl-s-triazine

4 $n = 3$

5 $n = 1$

10 6 $n = 2$

7 Run 6 deviated from the standard procedure in that: 1) Silux™ restorative, commercially available from 3M, was used in place of the P-50™ restorative called for in the adhesive strength test method; and 2) the polymer (VBP) had 75% of the customary methacrylate functionality of the precipitated dry polymer of EXAMPLE 11 of European
15 Published Pat. Application No. 0 323 120.

8 Run 7 deviated from the standard procedure in that Vitrebond™ glass ionomer cement (available from 3M) was used in place of the P-50™ restorative called for in the adhesive strength test method.

20 9 ("CPQ") = Camphorquinone.

10 ("DPICI") = Diphenyliodonium chloride.

The above data illustrates the adhesion to dentin or enamel obtained when a variety of primers are applied in a single application to the hard tissue. The above runs all
25 contained polymer, monomer and water. Runs 2, 3, 4 and 5 further contained maleic acid.

Example 2

Using the adhesive strength test method outlined above and Application Procedure I, the average shear strength on enamel of several primer compositions was evaluated. The
30 primers were formulated from aqueous solutions of various polymers, HEMA, and maleic acid as listed in Table 2. Each primer further contains 0.005 parts CPQ. The polymers used in this example were prepared by reacting VBP, MOSTOL, and TMDI. A solution of 69 parts tetrahydrofuran ("THF") and 6.0 parts MOSTOL was slowly added to a solution of 44.4 parts THF, 1.32 parts TMDI and 0.5 parts dibutyltin dilaurate
35 ("DBTDL") and heated at 40 °C for 18 hours with a dry air atmosphere. Four different

polymer formulations were prepared by reacting the above solution with VBP polymer. A "3%" triazine functionalized polymer (i.e., approximately 3% of the final polymer weight is represented by the triazine moiety) was prepared by slowly adding 0.75 parts triazine (i.e., not counting the weight attributable to the TMDI component or the solvent) to 25 parts VBP polymer. This reaction was run at 40 °C for 18 hours with DBTDL catalyst and a dry air atmosphere. The resultant polymer was precipitated into ethylacetate and dried in a vacuum oven to remove the solvent. Likewise, by varying the stoichiometry of the triazine and VBP, a 6%, 9%, and 12% triazine functionalized polymer was made. Set out below in Table 2 are the run number, ingredients, and the average shear strength to enamel.

Table 2

Run #	Maleic acid	HEMA	Water	Polymer, VBP-T	% Triazine on polymer	Adhesion to enamel, MPa.
1	0.251	1.582	3.060	0.342	6	12.1
2	0.126	2.071	2.497	0.434	9	16.2
3	0.250	2.552	1.918	0.523	6	11.2
4	0.127	1.078	3.349	0.582	3	13.0
5	0.375	1.072	3.340	0.582	3	15.6
6	0.252	1.470	2.791	0.760	0	8.5
7	0.250	1.445	2.795	0.760	12	11.5
8	0.000	1.442	2.807	0.760	6	7.4
9	0.251	1.446	2.792	0.761	6	15.0
10	0.500	1.444	2.793	0.761	6	13.0
11	0.249	0.692	3.406	0.924	6	12.0
12	0.249	1.203	2.292	1.524	6	7.0

Example 3

Using the adhesive strength test method outlined above and Application Procedure II, the average shear strength on dentin and enamel of several primer compositions was evaluated. The primers were formulated from aqueous solutions of VBP polymer, HEMA and maleic acid as listed in Table 3. The additional film former was comprised of 61.9 parts Bis-GMA, 37.1 parts HEMA, 0.25 parts CPQ, 0.25 parts diphenyliodonium hexafluorophosphate ("DPIHFP"), and 0.50 parts ethyl 4-dimethylaminobenzoate ("EDMAB"). Set out below in Table 3 are the run number, ingredients, and the average shear strength on enamel and dentin in MPa.

10

Table 3

	Run #	Maleic acid	HEMA	Water	Polymer, VBP	Adhesion to enamel, MPa.	Adhesion to dentin, MPa.
15	1	0.501	2.487	7.105	0.003	18.5	6.1
	2	0.507	1.029	8.451	0.032	23.5	7.9
	3	0.803	2.328	6.796	0.073	19.4	7.1
	4	0.527	2.405	7.006	0.077	20.1	13.6
20	5	0.202	2.484	7.229	0.080	15.8	17.8
	6	0.501	4.604	4.751	0.144	17.8	27.9
	7	0.324	1.301	8.133	0.236	26.6	16.4
	8	0.500	1.500	7.500	0.500	23.7	19.7
	9	0.329	3.290	5.805	0.588	21.3	26.8
25	10	0.502	1.244	7.005	1.243	23.8	15.1

Additional specimens of run 8 were prepared and stored in distilled water at 37 °C. At time intervals of seven days, one month, and three months, specimens were removed from the water and tested as described above. The average shear strength on dentin and enamel at each time is shown in Table 4 below.

Table 4

Time in 37 °C water	Adhesion to enamel, MPa.	Adhesion to dentin, MPa.
24 hr.	23.7	19.7
7 days	26.5	21.2
1 month	32.7	26.8
3 months	23.7	20.1

The above data (in Tables 3 and 4) illustrates the adhesion to dentin and enamel obtained when a variety of primers are employed through a single application to the hard tissue followed by an overcoat of additional film former. The data of Table 4 illustrates the excellent stability of the bond upon exposure to aqueous environments for a prolonged period.

Example 4

Using the adhesive strength test method outlined above and Application Procedure III, the average shear strength on dentin and enamel of a primer composition was evaluated. The etchant was comprised of 8 parts maleic acid and 92 parts water; the primer solution contained 13.3 parts VBP polymer, 39.8 parts HEMA, and 46.9 parts water; and the additional film former contained 61.9 parts Bis-GMA, 37.1 parts HEMA, 0.25 parts CPQ, 0.25 parts DPIHFP, and 0.50 parts EDMAB. The average shear strength on enamel and dentin was 27.7 MPa. and 16.8 MPa. respectively.

Examples 5 and 6

Using the adhesive strength test method outlined above and Application Procedure IV, the average shear strength on dentin and enamel of two primer compositions was evaluated. The etchant, primer, and additional film former of EXAMPLE 5 are the same as used in EXAMPLE 4. The primer and additional overcoat film former of EXAMPLE 6 were the same as in EXAMPLE 4, however, the etchant of EXAMPLE 6 was a phosphoric acid etching gel containing 35 parts phosphoric acid, 5.5 parts Cabosil (available from Degussa), 0.1 parts methylene blue, and 59.4 parts water. In a like manner to EXAMPLE 3, specimens were tested after storage in water at 37 °C for a period of up to one month.

The results are listed in Table 5 as a function of storage time.

Table 5

	Example	Time in 37 °C water	Adhesion to Enamel, MPa.	Adhesion to Dentin, MPa.
5	5	24 hr.	27.7	30.6
	5	7 days	19.5	29.3
10	5	1 month	28.4	24.1
	6	24 hr.	27.1	17.7
	6	7 days	31.4	11.2
	6	1 month	38.0	17.8

The data of Table 5 demonstrates that very acceptable average shear strengths can be achieved using primers that contain either maleic acid or phosphoric acid. The average shear strength to both dentin and enamel was durable and stable over a prolonged period.

Example 7

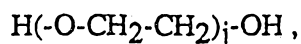
Adhesion to Sclerotic Dentin

The ability to bond to sclerotic dentin is an important feature lacking in currently available adhesive systems. In this example ten human dentin specimens which were characterized as sclerotic were treated using the adhesive strength test method outlined above and Application Procedure IV. The etchant, primer, and the additional film former were the same as used in EXAMPLE 4. The average adhesion value to sclerotic dentin was 17.3 MPa. while a Scotchbond™ 2 control adhesive (available commercially from 3M) provided an average shear strength of less than 3 MPa.

Example 8

Effect of Varying Molecular Weight

In this example a series of polyethyleneglycol polymers ("PEG") of varying molecular weights were "end-capped" with itaconic anhydride, with succinic anhydride or with 2-isocyanatoethyl methacrylate ("IEM"). PEG is represented by the following formula:



wherein the value of j for this series of PEG polymers (and their end-capped derivatives) is listed in Table 6. The preparation of the end-capped polymers involved the
 5 stoichiometric reaction of two equivalents of end capping agent to one equivalent of polymer. Itaconic anhydride or succinic anhydride was attached to the PEG molecule by heating the components at 90 °C as a neat solution (i.e., without solvent). The reaction was monitored by nuclear magnetic resonance until disappearance of the starting material at
 10 which time the heat was removed. IEM was attached to the PEG molecule by reacting the ingredients in a methylene chloride solution containing 0.4% dibutyltin dilaurate catalyst for 30 minutes at 90 °C. The solvent was removed by evaporation using a rotary evaporation apparatus.

Using the adhesive strength test method outlined above and Application Procedure
 15 IV, the shear strength on dentin and enamel of various primer compositions was evaluated. The etchant, and additional film former are the same as used in EXAMPLE 4. The primer was comprised of 10 parts of the indicated polymer (as listed in Table 6), 40 parts HEMA, and 50 parts water. Table 6 illustrates the average shear strength on enamel and dentin.

20

Table 6

	Run #	Ave. number of ethylene repeat groups (j)	Final approx. molecular weight (Mw)	End-cap moiety	Adhesion to enamel, MPa.	Adhesion to dentin, MPa.
25	1	6.4	300	none	11.3	14.7
	2	13.2	600	none	8.9	10.3
	3	33.7	1,500	none	18.6	11.8
	4	45	2,000	none	22.8	11.0
	5	77	3,400	none	17.6	12.2
30	6	181	8,000	none	13.1	13.1
	7	6.4	524	Ita. Anhyd.	15.1	20.5
	8	13.2	824	Ita. Anhyd.	21.2	16.0
	9	33.7	1,724	Ita. Anhyd.	17.8	20.6
35	10	45	2,224	Ita. Anhyd.	18.0	18.6
	11	77	3,624	Ita. Anhyd.	18.2	11.8

	12	181	8,224	Ita. Anhyd.	20.3	9.4
	13	6.4	500	Suc. Anhyd.	16.1	23.3
	14	13.2	800	Suc. Anhyd.	12.1	17.3
	15	33.7	1,700	Suc. Anhyd.	19.6	11.6
5	16	45	2,200	Suc. Anhyd.	10.1	15.6
	17	77	3,600	Suc. Anhyd.	18.8	9.1
	18	181	8,200	Suc. Anhyd.	12.2	10.0
	19	6.4	610	IEM	14.6	12.7
	20	13.2	910	IEM	16.9	10.4
10	21	33.7	1,810	IEM	26.3	11.4
	22	45	2,310	IEM	11.5	9.6
	23	77	3,710	IEM	23.2	10.5
	24	181	8,310	IEM	19.4	8.6

15

Example 9**Adhesion in High Humidity Environment**

This example demonstrates the ability of the compositions of the invention to bond to dentin under severe conditions of high humidity (i.e., relative humidity ("RH") > 90%). Using the adhesive strength test method outlined above and Application Procedure V, the average shear strength on dentin of various primer compositions was evaluated. The etchant and additional film former are the same as used in EXAMPLE 4. The primer for runs 2-9 contained 10 parts of the indicated polymer (as listed in Table 7), 40 parts HEMA, and 50 parts water. The primer for runs 10-12 contained 13.3 parts polymer, 39.8 parts HEMA, and 46.9 parts water. The primer of run 1, which is included as a control, is composed of 2.5 parts maleic acid, 58.5 parts HEMA, and 39.0 parts water and contains no polymer.

30

35

Table 7

	Run #	Polymer in the primer	Adhesion to dentin, MPa.	Mol. wt.	End capping group
	5				
	1	none ¹	< 2.5		
	2	Ex. 8, run 4	6.8	2,000	none
	3	Ex. 8, run 7	8.2	524	Ita. Anhyd.
	4	Ex. 8, run 9	5.3	1,724	Ita. Anhyd.
10	5	Ex. 8, run 10	9.2	2,224	Ita. Anhyd.
	6	Ex. 8, run 11	10.9	3,624	Ita. Anhyd.
	7	Ex. 8, run 12	5.7	8,224	Ita. Anhyd.
	8	Ex. 8, run 16	9.9	2,200	Suc. Anhyd.
	9	Ex. 8, run 22	11.7	2,310	IEM
15	10	VBP3:2 ²	7.0	8,900	
	11	VBP	22.4 ⁴	20,000	
	12	AA-IEM ³	16.5	115,000	

20 ¹Control experiment.

²("VBP3:2") = the precipitated dry polymer of EXAMPLE 11 of European Published Pat. Application No. 0 323 120 with a ratio of acrylic acid to itaconic acid of 3:2 instead of 4:1.

³("AA-IEM") = the precipitated dry polymer of EXAMPLE 10 of European Published Pat. Application No. 0 323 120.

⁴ Average of 15 strength values.

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Example 10**Effect of Polymer Concentration in the Primer**

This example demonstrates the ability of the compositions of the invention to bond to dentin under severe conditions of high humidity (RH > 90%). Using the adhesive strength test method outlined above and Application Procedure V, the average shear strength on dentin of various primer compositions was evaluated. The etchant, and additional film former are the same as used in EXAMPLE 4. The composition of the primer is listed in Table 8 and illustrates the effect of varying the amount of polymer from 0% (run #1) to 50% (run #9). As is evident from the adhesion values reported in Table 8 even small amounts of polymer drastically improve performance in a high humidity environment.

Table 8

Run#	HEMA	Water	Polymer, VBP	Adhesion to dentin, MPa.
1	40	60	0	0.0
2	40	59.95	0.05	8.1
3	40	59	1	20.8
4	40	55	5	17.4
5	40	50	10	20.0
6	40	40	20	22.1
7	40	30	30	14.6
8	40	20	40	16.3
9	30	20	50	13.6

Example 11

Using the adhesive strength test method outlined above and Application Procedure IV, the average shear strength on dentin and enamel of a primer composition was evaluated as a function of the standing time and the type of acid. The etchant contained either malic acid or phosphoric acid in water as listed in Table 9. The primer and the additional film former are the same as used in EXAMPLE 4. Table 9 illustrates the concentration of acid in the aqueous etchant for each run and the resultant average shear

strength to enamel and dentin.

Table 9

Run 5 #	Acid	% Acid in etchant	Standing time (sec.)	Adhesion to enamel, MPa.	Adhesion to dentin, MPa.
1	phosphoric	5.0	17.5	26.5	23.6
2	phosphoric	21.3	17.5	26.4	26.3
10 3	phosphoric	37.5	17.5	29.5	29.3
4	phosphoric	21.3	5.0	28.6	30.7
5	phosphoric	21.3	30.0	28.1	27.7
6	maleic	2.0	17.5	23.8	16.7
7	maleic	11.0	17.5	21.9	22.0
15 8	maleic	20.0	17.5	30.3	23.3
9	maleic	11.0	30.0	26.0	23.0
10	maleic	11.0	30.0	26.0	23.0

Example 12

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Comparison of Competitive Dentin Adhesives

This example compares the ability of a composition of this invention and several commercial dentin adhesive systems to bond to dentin under severe conditions of high humidity (RH > 90%). Using the adhesive strength test method outlined above and

25 Application Procedure V, the average shear strength on dentin of the composition of Run 2 of EXAMPLE 9 was compared to five commercially available dentin adhesive systems. The commercial products were applied to the prepared dentin as recommended by their respective manufacturers.

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Table 10(a)

Run#	Product	Adhesion to dentin, MPa.
5		
1	Run 2 of EXAMPLE 9	24.7
2	<u>XR</u> -Bond™ ¹	0.6
3	Universal Bond® ³ 2	2.9
4	Tenure™ ³	7.8
10	5 All-Bond™ ⁴	5.3
6	Scotchbond 2™ ⁵	2.9

- 1 XR-Primer™/XR-Bond™ Dentin/Enamel Bonding System available from Kerr Manufacturing Co. USA.
- 15 2 Prisma Universal Bond®³ Dentin/Enamel Bonding Agent available from L.D. Caulk Division Dentsply Int. Inc. Milford, Del.
- 3 Tenure™ Solution Dentin Bonding System available from Den-Mat Corp. Santa Maria, Ca.
- 20 4 All-Bond Universal Dental Adhesive System available from Bisco, Inc. Itasca, Ill.
- 5 Scotchbond 2™ Light Cure Dental Adhesive with Scotchprep™ Dentin Primer available from 3M Co. St. Paul, Mn.

The above commercial dentin adhesive systems were also modified by adding 10, 20, or 30% VBP to their respective primer component(s). The modified commercial products were then tested under conditions of high humidity using the adhesive strength test method outlined above and Application Procedure V. Table 10(b) lists the adhesion to dentin obtained and the percentage of VBP added to the primer or primers. The modified commercial products were applied to the prepared dentin as recommended by their respective manufacturers.

Table 10(b)

Run#	Product	% VBP	Adhesion to dentin, MPa.
5			
1	XR-Bond™	10	0.5
2	XR-Bond™	20	7.9
3	Universal Bond®3	10	0.0
4	Universal Bond®3	20	1.8
10	5 Universal Bond®3	30	0.5
6	Universal Bond®3 ¹	30	5.8
7	Tenure™	10	6.0
8	Tenure™	20	11.7
9	All-Bond II™2	10	15.7
15	10 All-Bond II™	20	10.1
11	All-Bond II™3	20	18.2

¹ In this run, the commercial primer was modified by adding 30% VBP and the adhesive of Run 2 Example 9 was substituted for the commercial Universal Bond adhesive.

² All-Bond II Dental Adhesive System available from Bisco, Inc. Itasca, Ill.

³ In this run, the commercial primer was modified by adding 20% VBP and the adhesive of Run 2 Example 9 was substituted for the commercial All Bond II adhesive.

Example 13

Using the adhesive strength test method outlined above and Application Procedure I, the average shear strength on dentin and enamel of several primer compositions was evaluated. A "tricure" ionomer composition was applied on top of the primer in place of the P-50™ restorative material. The tricure ionomer was prepared by mixing a powder and a liquid, described below, at a ratio of 2.2:1. The liquid was prepared by mixing the ingredients set out below in Table 11.

Table 11

	<u>Ingredients</u>	<u>(parts)</u>
	VBP	50
5	Water	30
	HEMA	20
	DPIHFP	1.0
	CPQ	0.25
	BHT	0.10

10 The powder contains a glass and two separate granular microcapsules. The glass was prepared by first mixing the ingredients set out below in Table 12. The ingredients were next melted in an arc furnace at about 1350-1450 °C, poured from the furnace in a thin stream and quenched using chill rollers to provide an amorphous single-phase fluoroaluminosilicate glass.

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Table 12

	<u>Ingredient</u>	<u>Amount</u>
	SiO ₂	37
	AlF ₃	23
20	SrO	20
	Al ₂ O ₃	10
	AlPO ₄	7
	Na ₂ AlF ₆	6
25	P ₂ O ₅	4

The glass was ball-milled to provide a pulverized frit with a surface area of 3.0 m²/g measured using the Brunauer, Emmet and Teller ("BET") method. Four parts "A-174" gamma-methacryloxypropyl trimethoxysilane (Union Carbide Corp.), 0.44 parts glacial acetic acid, 25 parts methanol, and 25 parts water were mixed for 15 minutes at room temperature, yielding a silanol-containing solution. One hundred parts of the above prepared glass were combined with the silanol treating solution, slurried for 1.5 hours at room temperature, dried overnight at 45 °C, and sieved through a 74 µm mesh screen.

Granular ascorbic-acid containing spherical microcapsules were formed by mixing 2.38 parts ascorbic acid in 47.62 parts water with 366 parts of a 1% solution of cellulose acetate butyrate in ethyl acetate. The mixture was maintained at 4 °C by immersing the

vessel in a ice-water bath and stirred at 700 rpm. 267 Parts of ice cold n-hexane were added to the solution over a thirty minute period. The granular precipitate was filtered, washed with ice cold n-hexane, dried under vacuum and then deagglomerated in an electric mill. Similarly, potassium persulfate containing spherical microcapsules were prepared by substituting $K_2S_2O_8$ for ascorbic acid.

Tricure powder was prepared by milling together for one hour 100 parts silanol treated glass, 0.55 parts ascorbic acid microcapsules, and 0.1 parts $K_2S_2O_8$ microcapsules.

Primers were made from aqueous solutions of various polymers, HEMA and optionally maleic acid as listed in Table 13. Set out below in Table 13 are the run number, ingredients, and the average shear strength value on enamel or dentin (in MPa.).

Table 13

<u>Ingredients</u>	<u>Run #</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
15 VBP	-	13.3	13.3	10	-	-	-	-
Polyacrylic acid ¹	-	-	-	-	25	-	-	-
HEMA	-	39.8	39.8	36	-	40	-	-
Water	92.0	46.9	138.9	54	75	60	100	
Maleic acid	8.0	-	8.0	-	-	-	-	-
20 <u>Adhesion (MPa.) at 24 hrs.</u>								
Enamel	11.8	15.8	12.0	16.9	6.2	-	-	
Dentin	-	10.7	10.4	10.1	3.7	4.5	5.3	

¹ 20,000 Mw available from B. F. Goodrich

As a control experiment the ionomer cement was applied directly to the hard tissue (i.e., no primer solution was used). The average shear strength on enamel and dentin was only 6.22 and 4.49 MPa. respectively for these specimens. Runs 5-7 are offered as comparative examples.

Example 14

Using the adhesive strength test method outlined above and Application Procedure I, the average shear strength on dentin and enamel of several primer compositions was evaluated. The primers contained 10 parts VBP, 54 parts water and 36 parts monomer as listed in Table 14. An ionomer composition, as described in EXAMPLE 13, was applied on top of the primer in place of the P-50 restorative material.

Table 14

Run#	Monomer	Adhesion to dentin, MPa.
1	HEMA	10.4
2	Glycerol dimethacrylate	10.1
3	Glycerol monomethacrylate	9.4
4	Pentaerythritol trimethacrylate	11.7

Five additional samples of run 1 were tested after thermo-cycling the specimens for over 600 cycles between 8 °C and 57 °C. The average shear strength for these specimens was 12.7 MPa.

The above data illustrates the adhesion to dentin obtained when various monomers were employed in the primer. The bond strengths were excellent and were stable upon exposure to thermo-cycling stresses.

Example 15

A copolymer was prepared by copolymerizing 28.8 parts acrylic acid and 13.0 parts itaconic acid as described in EXAMPLE 3 of European Published Pat. Application No. 0 323 120. Into another flask was charged 22.2 parts isophorone diisocyanate, 22.15 parts THF, 0.05 parts BHT and 0.2 parts DBTDL. The flask was fitted with a reflux condenser, stirrer and addition funnel. A solution of 13.0 parts HEMA dissolved in 22.15 parts THF was added dropwise. When the reaction was complete this solution was added to the copolymer solution previously prepared and allowed to react. The resultant derivitized copolymer was precipitated in ethyl acetate and dried in vacuo. Nuclear magnetic resonance ("NMR") and infrared ("IR") analysis showed the presence of the carboxyl and methacryloyl functional groups. A primer solution was made up by dissolving 1.4

parts of the above polymer in a mixture of 3.5 parts HEMA and 5.1 parts water. Using the adhesive strength test method outlined above and Application Procedure I, the shear strength on dentin and enamel of this primer composition was evaluated. An ionomer composition, as described in EXAMPLE 13, was applied on top of the primer in place of the P-50 restorative material. The average shear strength on enamel and dentin using this primer was 17.9 and 10.4 MPa. respectively, while the average shear strength of the ionomer directly on enamel and dentin (i.e., without the primer) was only 4.7 and 3.8 MPa. respectively.

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Example 16

Using the adhesive strength test method outlined above and Application Procedure I, the average shear strength on dentin and enamel of several primer compositions was evaluated. An ionomer composition, as described in EXAMPLE 13, was applied on top of the primer in place of the P-50 restorative material. The primers of this example contained 48 parts water, 40 parts HEMA, and 12 parts polymer as listed in Table 15. The polymers of runs 2-4 are essentially the same as VBP except the mole ratio of acrylic acid and itaconic acid was varied. The polymer of run 2 ("VBP7:3"), for example, contained 7 equivalents of acrylic acid to 3 equivalents of itaconic acid. This polymer also contained more IEM functionality than VBP.

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Table 15

Run#	Polymer	% Derivatization with IEM	M _w	Adhesion to dentin, MPa.
25				
1	VBP	16	18,000	9.17
2	VBP7:3	25	11,900	11.11
3	VBP3:2	34	9,150	9.94
30 4	VBP1:1	16	6,130	10.21

Various modifications and alterations of this invention will be apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not limited to the illustrative embodiments set forth herein.

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The claims defining the invention are as follows:

1. A method for adhering to or coating dentin, comprising the steps of:
 - (a) applying to said dentin adhesively effective amounts of an acid and a water-dispersible film former, wherein said film former comprises
 - 5 (i) a polymer having a weight average molecular weight of at least 1100 and
 - (ii) an adhesively effective amount of a polymerizable monomer wherein said acid, being different from said polymer, has a pKa less than or equal to that of phenol; and
 - (b) hardening said film former to provide adhesive shear strengths of at least 7
 10 MPa to dentin.
2. A method according to claim 1, wherein said acid and said film former are concurrently applied as a mixture to said dentin.
3. A method according to claim 1 or claim 2, wherein said film former further comprises water.
- 15 4. A method according to any one of claims 1 to 3, wherein said acid has a pKa between about -10 and about +5.
5. A method according to any one of claims 1 to 3, wherein said acid is selected from the group consisting of sulfonic acids, carboxylic acids, dicarboxylic acids, phosphonic acid, phosphoric acid, mineral acids and combinations thereof.
- 20 6. A method according to any one of claims 1 to 5, wherein said polymer has a weight average molecular weight in the range from 1,100 to 1,000,000.
7. A method according to claim 6, wherein said polymer has a weight average molecular weight in the range from 5,000 to 200,000.
8. A method according to any one of the preceding claims, wherein said polymer
 25 contains one or more polymerizable groups selected from the group consisting of acrylates, methacrylates and combinations thereof.
9. A method according to any one of claims 1 to 8, wherein said polymer is a polyalkenoic acid further containing addition polymerizable reactive groups.
10. A method according to claim 1 or claim 2, wherein said film former contains
 30 one or more substances having a sufficient number of water-dispersible groups to render said film former, exclusive of any water that may be present therein, dispersible or soluble in water to at least 5 weight percent.
11. A method according to claim 10, wherein said water-dispersible groups are selected from hydroxyl groups, carboxyl groups, sulfonic acid groups, cationic salts,
 35 amide linkages and polyether linkages.
12. A method according to claim 1 or claim 2, wherein said film former further comprises a cosolvent.
13. A method according to claim 1, wherein said polymerizable monomer contains one or more polymerizable groups selected from the group consisting of acrylate groups,
 40 methacrylate groups and combinations thereof.

14. A method according to claim 13, wherein said monomer is 2-hydroxyethylmethacrylate.

15. A method according to any one of the preceding claims, further comprising the steps of:

5 removing readily volatile solvents from said film former to leave a residual film on said dentin; and

overcoating said residual film with an additional film former prior to hardening said film former and said additional film former.

16. A method according to claim 15, wherein said additional film former is
10 capable of forming a homogeneous solution when combined with said residual film.

17. A method according to claim 15 or claim 16, wherein said film former and said additional film former are then overcoated with at least one layer of restorative material selected from the group consisting of composites, restoratives, hardenable coatings, glass ionomer cements and combinations thereof.

15 18. A method according to claim 1 or claim 2, wherein said film former contains one or more addition polymerizable groups, and prior to hardening said film former, readily volatile solvents are removed therefrom to leave a residual film that is then overcoated with a restorative and said film former being hardened using an autocuring or lightcuring polymerization catalyst.

20 19. A method according to claim 1, wherein said acid is sequentially applied to said dentin and rinsed or thinned from the dentin before application of said film former.

20. A method according to any one of the preceding claims, wherein said dentin is sclerotic dentin.

21. A method according to claim 1 or claim 2, wherein said application occurs in
25 a high humidity environment and provides an adhesive shear strength to dentin of at least 7 MPa.

22. A method according to claim 1 or claim 2, wherein said application occurs in a high humidity environment and provides an adhesive shear strength to dentin of at least 12 MPa.

30 23. A method according to claim 1 or claim 2, wherein said application provides an adhesive shear strength of at least 12 MPa.

24. A method for adhering to or coating dentin, comprising the steps of:

(a) applying to said dentin adhesively effective amounts of a water-dispersible film former comprising:

35 i) an adhesively effective amount of a polymer containing an acid functionality having a pKa less than or equal to that of phenol and having a weight average molecular weight of at least 1100;

ii) an adhesively effective amount of a polymerizable monomer; and

iii) water; and

(b) hardening said film former by exposing said film former to actinic radiation to provide adhesive shear strengths of at least 7 MPa.

25. A method for adhering to or coating dentin, comprising the steps of:

(a) applying to said dentin adhesively effective amounts of a water-dispersible
5 film former comprising:

i) an adhesively effective amount of a polymer containing an acid functionality having a pKa less than or equal to that of phenol and having a weight average molecular weight of at least 1100;

ii) an adhesively effective amount of a polymerizable monomer; and

10 iii) water; and

(b) hardening said film former by exposing said film former to actinic radiation wherein said application occurs in a high humidity environment and provides an adhesive shear strength of at least 5 MPa.

26. A method according to claim 24 or claim 25, wherein said polymer has a
15 weight average molecule weight in the range from 1,100 to 1,000,000.

27. A method according to claim 26, wherein said polymer has a weight average molecule weight in the range from 5,000 to 200,000.

28. A method according to any one of claims 24-27, wherein said polymerizable monomer is selected from the group consisting of 2-hydroxyethylmethacrylate,
20 hydroxypropylmethacrylate and methacrylic acid.

29. A method according to any one of claims 24-28, wherein said acid functionality is selected from the group consisting of alkylsulfonic acids, arylsulfonic acids, carboxylic acids, mineral acids, phenols and combinations thereof.

30. A method according to any one of claims 24-28, wherein said polymer is a
25 polyalkenoic acid containing addition polymerizable reactive groups.

31. A method according to any one of claims 24 to 30, wherein said dentin is sclerotic dentin.

32. A method according to any one of claims 1-8, wherein the polymer comprises an acid functionality selected from the group consisting of sulfonic acids, carboxylic acids, dicarboxylic acids, phosphonic acid, phosphoric acid, mineral acids, and
30 combinations thereof.

33. A method according to any one of claims 1-8, wherein the polymer comprises a phosphoric acid functionality.

34. A method for adhering to or coating hard tissue, comprising the steps of:

35 (a) applying to said hard tissue adhesively effective amounts of a water-dispersible film former comprising:

i) a polymer containing an acid functionality having a pKa less than or equal to that of phenol and having a weight average molecular weight of at least 1100;

ii) a polymerizable monomer; and

40 iii) water; and

(b) *hardening said film former by exposing said film former to actinic radiation, wherein said application occurs in a high humidity environment and provides an adhesive shear strength of at least 5 MPa.*

35. A method for adhering to or coating hard tissue, comprising the steps of:

5 (a) applying to said hard tissue adhesively effective amounts of an inorganic or organic acid and a water-dispersible film former, wherein said film former comprises:

(i) an adhesively effective amount of a polymer comprising a carboxylic acid functionality, and having a weight average molecular weight of at least 1100; and

10 (ii) an adhesively effective amount of a polymerizable monomer comprising an acrylate or methacrylate functionality;

wherein said acid, being different from said film former, has a pKa less than or equal to that of phenol; and

(b) hardening said film former to provide adhesive shear strengths of at least 7 MPa.

15 36. A method for adhering to or coating hard tissue, comprising the steps of:

(a) applying to said hard tissue adhesively effective amounts of an inorganic or organic acid and a water-dispersible film former, wherein said film former comprises

20 (i) an adhesively effective amount of a polymer comprising a polymerizable group selected from the group consisting of acrylates, methacrylates and combinations thereof, and having a weight average molecular weight of at least 1100; and

(ii) an adhesively effective amount of a polymerizable monomer comprising an acrylate or methacrylate functionality;

wherein said acid, being different from said film former, has a pKa less than or equal to that of phenol; and

25 (b) hardening said film former to provide adhesive shear strengths of at least 7 MPa.

37. A hardenable primer film, said film forming a layer with dentin whose surface has been modified by treatment with an acid having a pKa less than or equal to that of phenol, wherein prior to being hardened said film comprises adhesively effective amounts
30 of a water-dispersible film former comprising:

(i) a polymer having a weight average molecular weight of at least 1100, and

(ii) a polymerizable monomer,
said film being capable of providing an adhesive shear strength of at least 7 MPa.

35 38. A film according to claim 37, wherein said film further comprises an acid having a pKa less than or equal to that of phenol.

39. A film according to claim 38, wherein said polymer has a weight average molecular weight in the range from 1,100 to 200,000 and said acid has a pKa between about -10 and about +5 and is selected from the group consisting of sulfonic acids,

carboxylic acids, dicarboxylic acids, phosphonic acid, phosphoric acid, mineral acids and combinations thereof.

40. A film according to claim 37 or claim 38, wherein said polymer includes a hydrophilic group selected from the group consisting of amide linkages, carboxyl groups, salts, hydroxyl groups, polyether linkages, sulfonic acid groups and combinations thereof.

41. A film according to claim 37 or claim 38, wherein said polymer includes at least one of: an acid radical selected from the group consisting of carboxylic acids, mineral acids, phenols, alkylsulfonic acids and arylsulfonic acids; an acid radical salt; and an acid radical reactive derivative selected from the group consisting of acid anhydrides, acid halides and esters.

42. A film according to claim 37, wherein said polymer further contains one or more polymerizable groups selected from the group consisting of acrylates, methacrylates and combinations thereof.

43. A film according to claim 37, wherein said polymer is a polyalkenoic acid further modified by the incorporation of addition polymerizable reactive groups.

44. A film according to any one of claims 37 to 43, wherein said film former contains one or more substances having a sufficient number of water-dispersible groups to render said film former, exclusive of any water that may be present therein, soluble or dispersible in water to at least 5 weight percent.

45. A film according to claim 44, wherein said water-dispersible groups are selected from hydroxyl groups, carboxyl groups, sulfonic acid groups, cationic salts, amide linkages and polyether linkages.

46. A film according to claim 37 or claim 38, wherein said polymerizable monomer contains one or more polymerizable groups selected from acrylate groups, methacrylate groups and combinations thereof.

47. A film according to claim 46, wherein said film former comprises 2-hydroxyethylmethacrylate.

48. A film according to claim 37, wherein said polymer further contains an acid functionality having pKa less than or equal to that of phenol.

49. A film according to claim 48, wherein said polymer has a weight average molecular weight in the range from 1,100 to 1,000,000.

50. A film according to claim 48, wherein said polymer has a weight average molecular weight in the range from 5,000 to 200,000 and wherein said film is capable of providing an adhesive shear strength when applied in a high humidity environment of at least 7 MPa.

51. A hardenable primer film according to any one of claims 48 to 50, wherein said film further comprises a monomer, oligomer or cosolvent.

52. A hardenable primer film according to claim 50, wherein said acid functionality has a pKa between about -10 and about +5 and is selected from the group

consisting of alkylsulfonic acids, arylsulfonic acids, carboxylic acids, mineral acids, phenols and combinations thereof.

53. A hardenable primer film, said film forming a layer with dentin whose surface has been modified by treatment with an acid having a pKa less than or equal to that of phenol, wherein prior to being hardened said film comprises adhesively effective amounts of a water-dispersible film former comprising:

(i) a polymer having a weight average molecular weight of at least 1100, and

(ii) a polymerizable monomer,

wherein said film is capable of providing an adhesive shear strength when applied in a high humidity environment of at least 5 MPa.

54. A hardenable primer film according to claim 53, wherein said film further comprises an acid having a pKa less than or equal to that of phenol.

55. A hardenable primer film according to claim 54 wherein said acid, being present in an adhesively effective amount, has a pKa between about -10 and about +5.

56. A hardenable primer film according to claim 38, wherein said film is capable of providing an adhesive shear strength when applied in a high humidity environment of at least 7 MPa and said acid, being present in an adhesively effective amount, has a pKa between about -10 and about +5.

57. A hardenable primer film according to claim 38, wherein said film is capable of providing an adhesive shear strength when applied in a high humidity environment of at least 12 MPa and said acid, being present in an adhesively effective amount, has a pKa between about -10 and about +5.

58. A hardenable primer film according to claim 38, wherein said film is capable of providing an adhesive shear strength of at least 12 MPa and said acid, being present in an adhesively effective amount, has a pKa between about -10 and about +5.

59. A film according to claim 37, wherein the polymer comprises an acid functionality selected from the group consisting of sulfonic acids, carboxylic acids, dicarboxylic acids, phosphonic acid, phosphoric acid, mineral acids, and combinations thereof.

60. A film according to claim 37, wherein the polymer comprises a phosphoric acid functionality.

61. A kit for adhering to or coating hard tissue, comprising:

a water dispersible primer comprising adhesively effective amounts of an acid having a pKa less than or equal to that of phenol and a film former comprising a polymer having a weight average molecular weight of at least 1100 and a polymerizable monomer; and

one or more of the dental materials selected from the group consisting of restoratives, adhesives, acid etchants, cements and sealants.

62. A kit for adhering to or coating hard tissue, comprising:

a water dispersible primer comprising adhesively effective amounts of a film former comprising (i) a polymer containing an acid functionality having a pKa less than or equal to that of phenol and having a weight average molecular weight of at least 1100 and (ii) a polymerizable monomer; and

5 one or more of the dental materials selected from the group consisting of restoratives, adhesives, acid etchants, cements and sealants.

63. A kit for adhering to or coating hard tissue, comprising:

(a) a water dispersible primer comprising adhesively effective amounts of a film former comprising a polymer having a weight average molecular weight of at least 1100
10 and a polymerizable monomer together with an acid etchant; and

(b) one or more of the dental materials selected from the group consisting of restoratives, adhesives, cements and sealants.

64. A kit for adhering to dentin comprising:

(a) an acid having a pKa less than or equal to that of phenol;

15 (b) ^{water dispersible} a film former comprising a polymer having a weight average molecular weight of at least 1100 and a polymerizable monomer; and

(c) one or more of the dental materials selected from the group consisting of restoratives, adhesives, cements and sealants.

65. A kit according to any one of claims 61-64, wherein said polymer has a
20 weight average molecular weight in the range of 1,100 to 1,000,000.

66. A kit according to any one of claims 61-64, wherein said kit provides adhesive shear strength to dentin, when applied in a high humidity environment, of at least 5 MPa.

67. A kit according to any one of claims 61-64, wherein said kit provides adhesive shear strength to dentin, when applied in a high humidity environment, of at least 7 MPa.

25 68. A kit according to any one of claims 61-64, wherein said kit provides adhesive shear strength to dentin, when applied in a high humidity environment, of at least 12 MPa.

69. A kit according to any one of claims 61-64, wherein said kit provides adhesive shear strength to dentin of at least 12 MPa.

30 70. A method for adhering an orthodontic bracket to enamel, comprising the steps of:

(a) applying to said enamel adhesively effective amounts of an acid and a water-dispersible film former, wherein said film former comprises

(i) an adhesively effective amount of a polymer having a weight average
35 molecular weight of at least 1100 and

(ii) an adhesively effective amount of a polymerizable monomer, and wherein said acid, being different from said polymer, has a pKa less than or equal to that of phenol;

(b) hardening said film former; and

(c) adhering an orthodontic bracket to said enamel having film former applied thereto.

71. A method for adhering to or coating dentin, substantially as described herein with reference to any one of the Examples other than comparative examples.

5 72. A hardenable primer film, substantially as described herein with reference to any one of the Examples other than comparative examples.

73. A method for adhering an orthodontic bracket to enamel, substantially as described herein with reference to any one of the Examples other than comparative examples.

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Dated 3 June, 1997
Minnesota Mining and Manufacturing Company

Patent Attorneys for the Applicant/Nominated Person
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/11290

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 A61K6/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A61K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 234 934 (MINNESOTA MINING AND MANUFACTURING COMPANY) 2 September 1987 see page 2, line 62 - page 5, line 4; claims; examples	1-57
Y	---	58-65
X	US,A,4 645 456 (J. JAMES) 24 February 1987 see column 1, line 65 - column 3, line 55; claims; example 3	1-57
Y	---	58-65
	GB,A,2 217 989 (IMPERIAL CHEMICAL INDUSTRIES) 8 November 1989 see page 16, paragraph 1; claim 22 ---	
	-/--	
¹⁰ Special categories of cited documents : ¹⁰ ^{"A"} document defining the general state of the art which is not considered to be of particular relevance ^{"E"} earlier document but published on or after the international filing date ^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) ^{"O"} document referring to an oral disclosure, use, exhibition or other means ^{"P"} document published prior to the international filing date but later than the priority date claimed ^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention ^{"X"} document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step ^{"Y"} document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu- ments, such combination being obvious to a person skilled in the art. ^{"&"} document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 22 MARCH 1993	Date of Mailing of this International Search Report 07.04.93	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer G.COUSINS-VAN STEEN	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	EP, A, 0 305 083 (MINNESOTA MINING AND MANUFACTURING COMPANY) 1 March 1989 -----	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9211290
SA 68905

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 22/03/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0234934	02-09-87	US-A- 4719149	12-01-88
		AU-B- 586319	06-07-89
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