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(12) (19) (CA) **Demande-Application**

(21) (A1) **2,216,471**
(86) 1996/03/06
(87) 1996/10/17

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(51) Int.Cl.[6] C07F 5/02, C08F 20/00, C09J 4/02, B32B 27/32, C08F 4/52, B32B 7/12
(30) 1995/04/14 (08/422443) US

(54) **COMPLEXES ORGANOBORANE/POLYAMINE ET COMPOSITIONS ADHESIVES A BASE DE CES COMPLEXES**

(54) **ORGANOBORANE POLYAMINE COMPLEXES AND ADHESIVE COMPOSITIONS MADE THEREWITH**

(57) Le complexe selon l'invention contient de l'organoborane et une polyamine. Cette polyamine est le produit de la réaction entre une substance à terminaison amine biprimaire et une substance présentant au moins deux groupes réagissant avec l'amine primaire. Ces complexes peuvent être utilisés dans des systèmes destinés à amorcer la polymérisation de monomères acryliques, et qui contiennent en outre une substance réagissant avec l'amine. L'on peut ainsi obtenir des compositions de monomères acryliques polymérisables utiles comme adhésifs.

(57) A complex comprises organoborane and polyamine. The polyamine is the reaction product of a diprimary amine-terminated material and a material having at least two groups reactive with primary amine. The complexes are useful in systems for initiating the polymerization of acrylic monomer, which systems further include a material reactive with amine. Polymerizable acrylic monomer compositions useful as adhesives can be prepared.

CA 02216471 1997-09-25

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) **International Patent Classification** 6 :
C07F 5/00, 5/02, C09J 4/00, C08F 220/00, B32B 7/12, C08F 291/00

A1

(11) **International Publication Number:** **WO 96/32397**

(43) **International Publication Date:** 17 October 1996 (17.10.96)

(21) **International Application Number:** PCT/US96/03015

(22) **International Filing Date:** 6 March 1996 (06.03.96)

(30) **Priority Data:**
08/422,443 14 April 1995 (14.04.95) US

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(81) **Designated States:** AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) **Title:** ORGANOBORANE POLYAMINE COMPLEXES AND ADHESIVE COMPOSITIONS MADE THEREWITH

(57) **Abstract**

A complex comprises organoborane and polyamine. The polyamine is the reaction product of a diprimary amine-terminated material and a material having at least two groups reactive with primary amine. The complexes are useful in systems for initiating the polymerization of acrylic monomer, which systems further include a material reactive with amine. Polymerizable acrylic monomer compositions useful as adhesives can be prepared.

ORGANOBORANE POLYAMINE COMPLEXES AND ADHESIVE COMPOSITIONS MADE THEREWITH

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates generally to organoborane polyamine complexes and, more specifically, to those complexes in which the polyamine is the reaction product of a diprimary amine-terminated material and a material having at least two groups reactive with primary amine. The invention further relates to the use of these complexes in systems for initiating the polymerization of acrylic monomers, as well as acrylic adhesive compositions made therewith. The adhesive compositions have excellent adhesion to a variety of substrates, especially low surface energy polymers.

Description of the Related Art

Organoboranes such as tributylborane and triethylborane have been reported to initiate and catalyze the polymerization of vinyl monomers (see, for example, G. S. Kolesnikov et al., Bull. Acad. Sci. USSR, Div. Chem. Sci. 1957, p. 653; J. Furakawa et al., Journal of Polymer Science, volume 26, issue 113, p. 234, 1957; and J. Furakawa et al., Journal of Polymer Science, volume 28, issue 116, 1958). The organoborane compounds of the type described in these references are

known to be quite pyrophoric in air which complicates facile use.

Chemical Abstracts No. 134385q (volume 80, 1974) "Bonding Polyolefin or Vinyl Polymers" reports that a mixture of 10 parts methyl methacrylate, 0.2 part tributylborane, and 10 parts poly(methylmethacrylate) was used to bond polyethylene, polypropylene and poly(vinyl acetate) rods.

U.S. Patent No. 3,275,611 to E. H. Mottus et al. discloses a process for polymerizing olefinic compounds with a catalyst comprising an organoboron compound, a peroxygen compound, and an amine. The organoboron compound and the amine may be added to the reaction mixture separately or they may be added as a preformed complex. The latter approach reportedly has the advantage of making the boron compound more easily handled, especially for certain boron compounds that tend to be pyrophoric in air but which are not pyrophoric when complexed. Especially useful boron catalysts are said to have the following general formulas: R_3B, $RB(OR)_2$, $R_2B(OR)$, R_2BOBR_2, R_2BX, and R_2BH, where R is preferably an alkyl radical having from 1 to 10 or more carbon atoms, and X is a halogen. Various amine complexing agents are mentioned although pyridine, aniline, toluidine, dimethylbenzylamine, and nicotine are used in the examples.

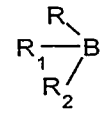
While Mottus et al. refer to polymerizing methacrylate monomers, there is no indication that the resulting polymers are useful as adhesives. Various acids are mentioned as monomers that may be polymerized

but there is no indication that an acid is a component of the polymerization initiator system.

British Patent Specification No. 1,113,722 "Aerobically Polymerisable Compositions," published May 15, 1968 discloses the polymerization of acrylate monomers through the use of a free-radical catalyst (e.g., peroxides) and triarylborane complexes having the general formula $(R)_3B$-Am wherein R is an aryl radical having from 6 to 12 carbon atoms and Am is an amine that can be selected from various classes such as alkylamines, cycloalklyamines, aralklyamines, polyamines (e.g., alkylene diamines and triamines), and heterocyclic amines. The polymerization is activated by heat or the addition of an acid. The resulting compositions are reportedly useful as adhesives.

Chemical Abstracts No. 88532r (volume 73, 1970) "Dental Self-curing Resin" and the full text paper to which it refers report that tributylborane can be made stable in air by complexing it with ammonia or certain amines (e.g., aniline, n-butylamine, piperidine, ethylenediamine) at a mole ratio of one and that the tributylborane can be reactivated with an amine acceptor such as an isocyanate, an acid chloride, a sulfonyl chloride, or anhydrous acetic acid. As a result, the complex can be used to polymerize blends of methyl methacrylate and poly(methylmethacrylate) to provide a dental adhesive. Tributylborane-ethylenediamine complexes and triethylborane-ammonia complexes, each with p-toluenesulfonyl chloride as the amine acceptor, are specifically mentioned.

A series of patents issued to Skoultchi and Skoultchi et al. (U.S. Patent Nos. 5,106,928, 5,143,884, 5,286,821, 5,310,835, and 5,376,746) disclose a two part initiator system that is reportedly useful in acrylic adhesive compositions, especially elastomeric acrylic adhesives. The first part of this two part system includes a stable organoborane amine complex and the second part includes a destabilizer or activator such as an organic acid or an aldehyde. The organoborane compound of the complex has the general formula:



where R, R_1 and R_2 are either alkyl groups having 1 to 10 carbon atoms or phenyl groups. Useful amines include n-octylamine, 1,6-diaminohexane, diethylamine, dibutylamine, diethylenetriamine, dipropylenediamine, 1,3-propylenediamine, and 1,2-propylenediamine.

The adhesive compositions are reportedly particularly useful in structural and semi-structural applications such as speaker magnets, metal-metal bonding, (automotive) glass-metal bonding, glass-glass bonding, circuit board component bonding, selected plastic to metal, glass, wood, etc. bonding, and electric motor magnets. Those plastics that may be bonded are not further described.

An efficient, effective means for adhesively bonding low surface energy plastic substrates such as polyethylene, polypropylene and polytetrafluoroethylene (e.g., TEFLON) has long been sought. The difficulties

in adhesively bonding these materials are well known. See, for example, "Adhesion Problems at Polymer Surfaces" by D.M. Brewis that appeared in Progress in Rubber and Plastic Technology, volume 1, page 1 (1985). The conventional approaches typically function by: (1) increasing the surface energy of the substrate (to more closely match the surface energies of the substrate and the adhesive thereby promoting better wetting of the substrate by the adhesive) and/or (2) eliminating additives and low molecular weight polymer fractions in the substrate that can migrate to the substrate surface and adversely affect adhesion by forming a weak boundary layer.

As a result, the conventional approaches often use complex and costly substrate surface preparation techniques such as flame treatment, corona discharge, plasma treatment, oxidation by ozone or oxidizing acids, and sputter etching. Alternatively, the substrate surface may be primed by coating it with a high surface energy material. However, to achieve adequate adhesion of the primer, it may be necessary to first use the surface preparation techniques described above. All of these techniques are well known, as reported in Treatise on Adhesion and Adhesives (J.D. Minford, editor, Marcel Dekker, 1991, New York, volume 7, pages 333 to 435). The known approaches are frequently customized for use with specific substrates. As a result, they may not be useful for bonding low surface energy plastic substrates generally.

Moreover, the complexity and cost of the presently known approaches do not render them particularly

suitable for use by the retail consumer (e.g., home repairs, do-it-yourselfers, etc.) or in low volume operations. One vexing problem is the repair of many inexpensive everyday household articles that are made of polyethylene, polypropylene or polystyrene such as trash baskets, laundry baskets and toys.

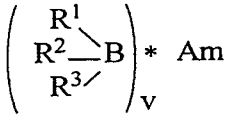
Consequently, there has been a considerable and long felt need for a simple, easy to use adhesive that can readily bond a wide variety of substrates, especially low surface energy materials, such as polyethylene, polypropylene and polytetrafluoroethylene, without requiring complicated surface preparation, priming and the like. It would also be considered useful for the adhesive to be able to bond a wide variety of diverse surfaces, including metals.

While an adhesive that can bond low surface energy plastics is certainly advantageous, the commercial utility of such an adhesive would be enhanced if the components thereof could be combined in a convenient mix ratio. This would permit facile application of the adhesive using conventional adhesive dispensers without the need for laborious hand weighing and mixing of the different components. However, the convenient mix ratio should not come at the expense of significantly reduced storage stability or performance. Thus, there is not only a need for an adhesive that can bond low surface energy plastics, but a need for such an adhesive that can be readily blended in a convenient mix ratio without a material reduction in storage stability or performance.

SUMMARY OF THE INVENTION

The invention relates to organoborane polyamine complexes and, more particularly, to such complexes wherein the polyamine is the reaction product of a diprimary amine terminated-material and a material having at least two groups reactive with primary amine, the number of primary amine groups in the reaction mixture being greater than the number of groups reactive with primary amine. The complexes can be used in systems that initiate the polymerization of acrylic monomer to yield acrylic adhesive compositions. The acrylic adhesive compositions have excellent adhesion to a wide variety of substrates but are especially useful for bonding low surface energy plastics (e.g., polyethylene, polypropylene, polytetrafluoroethylene, etc.) that, heretofore, have been bonded using complex and costly surface preparation techniques.

In general, complexes of the invention have the structure:



R^1 is an alkyl group having 1 to 10 carbon atoms. R^2 and R^3 are independently selected from alkyl groups having 1 to 10 carbon atoms and phenyl-containing groups. Preferably, R^1, R^2 and R^3 are independently selected alkyl groups having 1 to 5 carbon atoms. Most preferably, they are the same.

The polyamine, Am, may be represented by the general strucutre E-$(L\text{-}E)_z$-L-E in which each E group is

the residue of the diprimary amine-terminated material and each L is a linking group that is the residue of the material having at least two groups reactive with primary amine. The integral value of z is ≥ 0 (more preferably, it is from 0 to 5, and most preferably it is 0 or 1). In preferred structures, the polyamine is substantially linear.

Useful diprimary amine-terminated materials include polyoxyalkylenediamines such as those having the structure $H_2NR^4O-(R^5O)_w—(R^6O)_x—(R^5O)_y—R^4NH_2$ wherein R^4, R^5, and R^6 are alkylene groups having 1 to 10 carbon atoms and which may be the same or which may be different; w is ≥ 1; x is ≥ 0; and y is ≥ 0. More preferably, R^4 is an alkyl group having 2 to 4 carbon atoms, R^5 is an alkyl group having 2 or 3 carbon atoms, and R^6 is an alkyl group having 2 or 3 carbon atoms.

Also useful as the diprimary amine-terminated material are linear alkyldiamines in which the alkyl group has from 1 to 12 carbon atoms.

Suitable candidates for the material having at least two groups reactive with primary amine may be represented by the general structure Y-R-Z, wherein Y and Z are moieties independently selected from the group consisting of carboxylic acid, carboxylic acid halide, ester, aldehyde, epoxide, amino alcohol, and acrylic, and R is a divalent organic radical. Most preferably Y and Z are the same.

The value of v is selected so as to provide an effective ratio of primary amine nitrogen atoms to boron atoms in the complex. The ratio of primary amine nitrogen atoms to boron atoms in the complex should

broadly be about 0.5:1 to 4:1, preferably about 1:1 to 2:1, more preferably about 1:1 to 1.5:1, and most preferably about 1:1.

Organoborane polyamine complexes of the invention can be used in systems that are capable of initiating the polymerization of acrylic monomer. In addition to organoborane polyamine complexes such as those described above, these systems further comprise an effective amount of a compound that is reactive with amine for liberating the organoborane. A wide variety of organoborane liberating compounds may be used including isocyanates, acids, acid chlorides, sulfonyl chlorides and aldehydes. Useful acids include Lewis acids and Bronsted acids, although acrylic acid and methacrylic acid are preferred. The amount of organoborane liberating compound is preferentially stoichiometric with the equivalents of amine in the polyamine but larger amounts may be used, for example, twice stoichiometric. Where an acid provides the organoborane liberator compound, a useful amount is in the range of about 100 to 350 mole %, more preferably about 150 to 250 mole % of the total equivalents of amine in the polyamine.

Consequently, the invention also relates to a polymerizable acrylic composition that comprises at least one acrylic monomer, an effective amount of an organoborane polyamine complex of the invention, and an effective amount of a compound that is reactive with amine (such as those described above) for liberating the organoborane to initiate polymerization of the at least one acrylic monomer.

A wide variety of acrylic monomers may be used but those which are preferred include monofunctional acrylate ester, monofunctional methacrylate ester, substituted derivatives of the foregoing, and blends of the foregoing. Methacrylate esters are especially useful, particularly desirable examples of which include methyl methacrylate, ethyl methacrylate, methoxy ethyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, cyclohexyl methacrylate, tetrahydrofurfuryl methacrylate, and blends thereof. Blends of alkyl methacrylate (e.g., methyl methacrylate) and alkyl acrylate (especially those in which the alkyl group has from 4 to 10 carbon atoms, e.g., butyl acrylate) are also quite useful.

Acrylic compositions of the invention are uniquely useful in providing adhesives, and adhesive compositions of the invention provide excellent adhesion to low surface energy polymeric or plastic substrates that historically have been very difficult to bond. Adhesion to low surface energy polymeric substrates is enhanced when the adhesive composition comprises about 0.03 to 1.5 weight % boron, more preferably about 0.1 to 0.3 weight % boron.

Consequently, in another aspect, the invention relates to a composite article comprising a first substrate, and a second substrate bonded to the first substrate by an acrylic adhesive composition according to the invention. Either or both substrates may be a low surface energy polymer or plastic such as polyethylene, polypropylene or polytetrafluoroethylene.

In another aspect, the invention relates to a method of initiating the polymerization of an acrylic monomer, the method comprising the steps of providing at least one acrylic monomer, blending the at least one acrylic monomer with a polymerization initiator system according to the invention, and initiating polymerization of the at least one acrylic monomer.

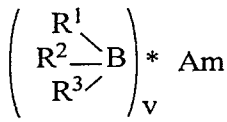
The invention further relates to a method of bonding a low surface energy polymer to a substrate. The method comprises the steps of providing a low surface energy polymer, providing a substrate, providing an adhesive composition according to the invention, applying the adhesive composition to either the low surface energy polymer or the substrate, joining the low surface energy polymer and the substrate with the adhesive composition therebetween, and permitting the adhesive composition to cure to adhesively bond the low surface energy polymer and the substrate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a broad aspect, this invention relates to organoborane polyamine complexes, particularly those complexes in which the polyamine comprises the reaction product of one or more diprimary amine-terminated materials (i.e., the two terminal groups are primary amine) and one or more materials containing at least two groups reactive with primary amine (the latter sometimes being referred to herein as a "difunctional primary amine-reactive" material). The complexes are especially useful in providing systems for initiating

the polymerization of acrylic monomers. Acrylic adhesives can be produced using the organoborane polyamine complexes of the invention. The acrylic adhesives can bond a wide variety of substrates, but provide exceptionally good adhesion to low surface energy plastic substrates (e.g., polyethylene, polypropylene, polytetrafluoroethylene, etc.) that, heretofore, have been bonded using complex and costly surface preparation techniques.

The complexes of the invention preferably have the following general structure:



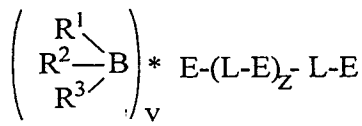
where R^1 is an alkyl group having 1 to 10 carbon atoms, and R^2 and R^3 are independently selected from alkyl groups having 1 to 10 carbon atoms and phenyl-containing groups. More preferably, R^1, R^2 and R^3 are alkyl groups having 1 to 5 carbon atoms such as methyl, ethyl, propyl, iso-propyl, n-butyl, iso-butyl, and pentyl. In general, shorter carbon chain lengths are preferred for the R^1, R^2 and R^3 groups as this promotes enhanced stability of the complex in air. Smaller, less bulky substituents are also preferred as larger, more bulky groups may negatively affect the adhesion provided by adhesives made therewith. By "independently selected" it is meant that R^2 and R^3 may be the same or that they may be different. R^1 may be the same as R^2 or R^3, or it may be different. Preferably R^1, R^2 and R^3 are the same. Most preferred are complexes in which R^1, R^2 and R^3 are each ethyl groups.

The value of v is selected so as to provide an effective ratio of primary amine nitrogen atoms to boron atoms in the complex, as explained more fully hereinbelow. The primary amine nitrogen atom to boron atom ratio in the complex is broadly about 0.5:1 to 4:1. Preferably, however, the ratio is about 1:1 to 2:1, more preferably about 1:1 to 1.5:1, and most preferably about 1:1. A primary amine nitrogen atom to boron atom ratio of less than 0.5:1 leaves free organoborane, a material that tends to be pyrophoric. At primary amine nitrogen atom to boron atom ratios in excess of 2:1, the practical utility of the complex in, for example, an adhesive system diminishes as the amount of complex that must be employed to generate a useful adhesive becomes larger. In addition, at high primary amine nitrogen atom to boron atom ratios, the amount of agent that must be added to react with the polyamine so as to liberate organoborane (to initiate polymerization) also becomes larger. The additional reactants could complicate the adhesive system.

The polyamine resulting from the reaction of diprimary amine-terminated material and difunctional primary amine-reactive material is substantially linear and preferably has the following general structure

$$E-(L-E)_z-L-E.$$

Consequently, complexes of the invention may be shown by the following general structure



wherein R^1, R^2 and R^3 are as defined above. Each E is the residue of the diprimary amine-terminated material and each L is a linking group that is the residue of the difunctional primary amine-reactive material. (By "residue" is meant those portions of the diprimary amine-terminated material and the difunctional primary amine-reactive material that remain after reaction to form the polyamine adduct.) The E and L groups are independently selected. That is, each E group may be the same or may be different, as may each L group, although it is preferred that each E group be the same and that each L group be the same. Preferably E and L are selected so as to form a complex that is soluble in acrylic monomer.

The majority (more than 50%) of the terminal groups in the polyamine should be primary amine. Some of the terminal groups may be provided by secondary amine, although an increasing proportion of non-primary amine terminal groups tends to reduce the stability of the resulting organoborane polyamine complex, which ultimately could be manifested in a complex that is pyrophoric. The polyamine may contain secondary and tertiary amine that are internal to the polyamine so long as the resulting complex is not overly weak which could result in a pyrophoric complex. The formation of a polyamine having a majority of primary amine terminal groups is promoted by employing a reaction

stoichiometry in which the number of E precursor functional groups (i.e., primary amines) is greater than the number of L precursor functional groups (i.e., primary amine-reactive groups).

The value of z is selected so as to provide both a polyamine and a complex of useful viscosity. As the value of z increases, the viscosity of the polyamine may become too high for easy mixing and handling. The polyamine preferably is a room temperature liquid and has a viscosity of less than about 200,000 cP at room temperature (more preferably about 20,000 cP or less) so as to yield a complex that is also a liquid at room temperature.

The value of z also influences the viscosity of the resulting organoborane polyamine complex. In two-part acrylic adhesives of the type described below (where the complex provides one part and the acrylic monomer provides the other part), the viscosity of the two parts is desirably about the same so as to promote easy mixing and dispensing of the adhesive.

In view of these parameters, the value of z may be greater than or equal to zero, although a value of about 0 to 5 is more preferred, and a value of 0 or 1 is most preferred. The actual value of z will depend on the particular organoborane as well as the composition to which the complex is to be added.

Diprimary amine-terminated materials promote the formation of substantially linear polyamine. Preferably, the diprimary amine-terminated material is a liquid although solid materials may be used. The diprimary amine-terminated material may be alkyl

diprimary amine, aryl diprimary amine, alkaryl diprimary amine, a polyoxyalkylenediamine, or mixtures thereof.

Polyoxyalkylenediamines are especially preferred and may have the following general structure:

$$H_2NR^4O-(R^5O)_w-(R^6O)_x-(R^5O)_y-R^4NH_2$$

R^4 and R^5 are alkylene groups having 1 to 10 carbon atoms and may be the same or may be different. Preferably, R^4 is an alkyl group having 2 to 4 carbon atoms such as ethyl, n-propyl, iso-propyl, n-butyl or iso-butyl. Preferably, R^5 and R^6 are an alkyl groups having 2 or 3 carbon atoms such as ethyl, n-propyl or iso-propyl.

The value of w is ≥ 1, more preferably about 1 to 150, and most preferably about 1 to 20. Structures in which w is 2, 3 or 4 are useful too. The value of x and y are both ≥ 0. It is preferred that the values of w, x, and y be chosen such that both the polyoxylalkylenediamine and the resulting complex are liquids at room temperature. Molecular weights of less than about 5,000 may be used, although molecular weights of about 1,000 or less are more preferred, and molecular weights of about 250 to 1,000 are most preferred.

Examples of particularly preferred polyoxyalkylenediamines include polyethyleneoxidediamine, polypropyleneoxidediamine, diethyleneglycolpropylenediamine, triethyleneglycolpropylenediamine, polytetramethyleneoxidediamine, and polyethyleneoxide-co-polypropyleneoxidediamine.

Examples of suitable commercially available polyoxyalkylenediamines include various JEFFAMINES from Huntsman Chemical Company such as the D, ED, and EDR series diamines (e.g., D-400, D-2000, D-5000, ED-600, ED-900, ED-2001, and EDR-148), as well as H221 from Union Carbide Company.

Useful alkyl diprimary amines include those having the structure NH_2-R-NH_2 wherein R is a linear alkyl group having about 1 to 12 carbon atoms such as 1,3-propane diamine, 1,6-hexanediamine, and 1,12-dodecanediamine. Other useful alkyl diprimary amines include triethylene tetraamine and diethylene triamine, which compounds illustrate that diprimary amines suitable for the invention may contain amine groups that are not primary. Examples of useful aryl diprimary amines include 1,3- and 1,4-phenylene diamine as well as the various isomers of diaminonaphthalene. An example of a useful alkylaryl diprimary amine is m-tetramethylxylene diamine.

Difunctional primary amine-reactive materials contain at least two groups reactive with primary amine. The reactive groups may be different, but it is preferred that they be the same. Difunctional primary amine-reactive materials should be free of groups that could hinder the formation of the organoborane polyamine complex by interfering with the reaction between the terminal primary amine groups of the polyamine and the organoborane.

Difunctional primary amine-reactive materials having a functionality of 2 (i.e., two groups reactive with primary amine) are preferred as this promotes the

formation of polyamine that is substantially linear. By "substantially linear" it is meant that the polyamine may contain some branching but without forming an interconnected network. If the polyamine is a solid, it remains fusible. Thus, useful materials may have a functionality greater than 2 but preferably a functionality that is less than 3.

Useful difunctional primary amine-reactive materials may be generally represented by the formula Y-R-Z wherein R is a divalent organic radical such as an alkyl, aryl or alkaryl group or combination thereof, and Y and Z are groups reactive with primary amine and which may be the same or may be different. Examples of useful Y and Z groups reactive with primary amine include carboxylic acid (-COOH), carboxylic halide acid (-COX, where X is a halogen, for example chlorine), ester (-COOR), aldehyde (-COH), epoxide (), amine alcohol ($-NHCH_2OH$), and acrylic ().

Suitable carboxylic acid-functional materials are preferably those which are useful in forming polyamides, for example, cyclohexane-1,4-dicarboxylic acid and dicarboxylic acids having the structure HOOC-R-COOH in which R is a linear alkyl group having about 2 to 21 carbon atoms. Also useful are dimer acids (i.e., the dimerization product of naturally occurring unsaturated fatty acids). Aromatic dicarboxylic acids (e.g., terephthalic and isophthalic acids) may be used

as can alkaryl dicarboxylic acids, especially in combination with alkyl dicarboxylic acids.

Examples of useful, commercially available polyamines derived from carboxylic acid-functional materials include the "Versamids" and "Genamids" from Henkel GmbH, and the "Ancamides" from Anchor Chemical Company.

Useful carboxylic acid halide-functional materials and ester-functional materials include those which are obtained by derivatizing the above-described carboxylic acid-functional materials.

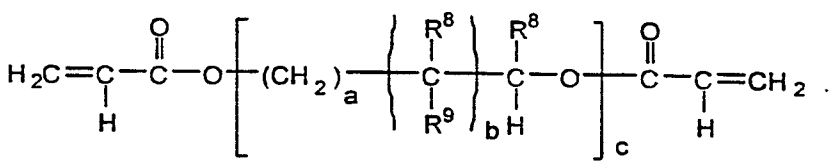
Suitable aldehyde-functional materials include alkyl, aryl or alkaryl dialdehydes such as oxaldehyde propanedialdehyde, succinaldehyde, adipaldehyde, 2-hydroxyhexanedial,; phthalaldehyde, 1,4,benzenediacetaldehyde, 4,4(ethylenedioxy) dibenzaldehyde, and 2,6-naphthalene dicarbaldehyde. Most preferred are glutaraldehyde and adipaldehyde.

Suitable epoxide-functional materials include aliphatic, cycloaliphatic and glycidyl ether diepoxides. Examples of cycloaliphatic diepoxides include vinylcyclohexene dioxide, 3,4-epoxycyclohexylmethyl 3,4-epoxycyclohexanecarboxylate, 3,4-epoxy-6-methylcyclohexylmethyl 3,4-epoxy-6-methylcyclohexanecarboxylate, bis(3,4-epoxy-6-methylcyclohexylmethyl)adipate, and aliphatic epoxy modified with polypropylene glycol and dipentene dioxide. Useful gylcidyl ether diepoxides include diglycidyl ether of bis-phenol A, diglycidyl ether of bis-phenol F, 1,4-butanediol diglycidyl ether, poly glycidyl ether of phenol formaldehyde resole or novolac

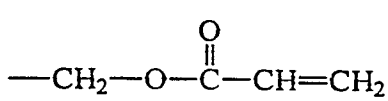
resin, and resorcinol diglycidylether. An example of a heterocyclic epoxide group-functional material is 1,3-(2,3-epoxy propyl-5,5- dimethyl-2,4-imidazolinedione). Examples of other useful diepoxides include polyglycol diepoxides, polyacrylate diepoxides, and urethane modified diepoxides. A wide variety of epoxy resins are listed in "Epoxy Resins-Chemistry and Technology" C.A. May, Ed. pp. 52-67, Marcel Dekker, NY 1988. Most preferred are the diepoxides based upon bis-phenol A and bis-phenol F.

Examples of useful amine alcohols are the amino resins available from Cytec Corp. known as "Beetle" and "Cymel".

Useful acrylic-functional materials are preferably diacrylates and a wide variety of such materials may be successfully employed in the complexes of the invention. Included among these are diacrylates having the following structure:



R^8 may be selected from the group consisting of hydrogen methyl, ethyl, $-CH_2OH$, and

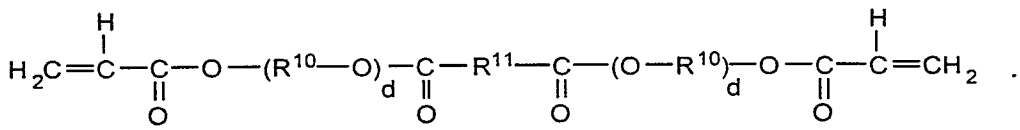


R^9 may be selected from the group consisting of hydrogen methyl, ethyl, $-CH_2OH$. The value of a is an integer greater than or equal to 1, more preferably, from 1 to about 8, and most preferably from 1 to 4. The integral value of b is greater than or equal to 1, more

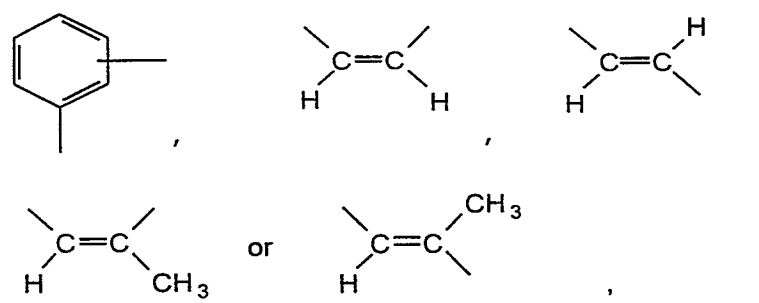
value of b is greater than or equal to 1, more preferably, from 1 to about 20. The value of c is 0 or 1.

Other diacrylates useful in forming polyamines for the complexes of the invention are ethylene glycol diacrylate, polyethylene glycol diacrylate, diglycerol diacrylate as well as other polyether diacrylates.

Other useful diacrylates have the general formula:



R^{10} may be an alkylene group with 2 to 6 carbon atoms; and R^{11} is $(CH_2)_e$ in which e is an integer of 0 to 8, or one of the following:

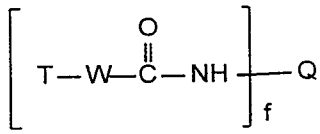


the phenyl group being substitutable at any one of the ortho, meta or para positions. The value of d is an integer of 1 to 4.

Typical materials of this class include diacrylate of bis(ethylene glycol) adipate, diacrylate of bis(ethylene glycol) maleate, diacrylate of

bis(ethylene glycol) phthalate, diacrylate of bis(tetraethylene glycol) phthalate, diacrylate of bis(tetraethylene glycol) sebacate, diacrylates of bis(tetraethylene glycol) maleate and the like.

Also useful as acrylic-functional materials are isocyanate-hydroxyacrylate or isocyanate-aminoacrylate reaction products. These may be characterized as acrylate terminated polyurethanes and polyureides or polyureas. Such precursors have the following general formula:

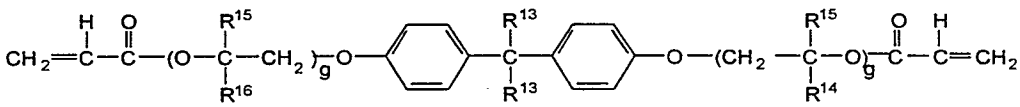


where W is selected from the group consisting of —O— and  . R^{12} is selected from the group consisting of hydrogen and lower alkyl groups (e.g., 1 to 7 carbon atoms). T is the organic residue of an active hydrogen-containing acrylic ester, the active hydrogen having been removed and the ester being hydroxy or amino substituted on the alkyl portion thereof. The integral value of f is from 1 to 6. Q is a mono- or polyvalent organic radical selected from the group consisting of alkyl, alkylene, alkenyl, cycloalkyl, cycloalkylene, aryl, aralkyl, alkaryl, poly(oxyalkylene), poly(carboalkoxyalkylene), and heterocyclic radicals, both substituted and unsubstituted.

Typical precursors of this class include the reaction product of mono- or polyisocyanates, for example, toluene diisocyanate, with an acrylate ester

containing a hydroxy or an amino group in the non-acrylate portion thereof, for example, hydroxyethyl acrylate.

Still another class of diacrylate L precursors useful in the present invention are the diacrylate esters of bisphenol type compounds. These monomers may be described by the following formula:



where R^{13} is hydrogen or methyl; R^{14} is hydrogen, methyl or ethyl; R^{15} is hydrogen, methyl or hydroxyl; R^{16} is hydrogen, chlorine, methyl or ethyl; and g is an integer having a value of 0 to 8. Representative monomers of the above-described class include diacrylate esters of 4,4'-bis-hydroxyethoxy-bisphenol A, diacrylate esters of bisphenol A, etc.

The polyamine can be readily manufactured by a condensation reaction. Polyamines based on acrylic or epoxide-functional materials can be easily prepared by mixing and heating the reactants to effect condensation. Polyamines based on carboxylic acid, ester or aldehyde-functional materials and which evolve water or methanol should be reacted under conditions that permit the water or methanol to be removed (e.g., by azeotropic or vacuum distillation). Polyamines based on carboxylic acid halide-functional materials should be reacted under conditions that permit the removal of the evolved hydrohalide acid (e.g., by adding an acid acceptor such as pyridine, the resulting hydrohalide acid salt of which can be removed by distillation).

Once the polyamine has been provided, the organoborane polyamine complex may be readily prepared using known techniques. Typically, the polyamine is combined with the organoborane in an inert atmosphere with slow stirring. An exotherm is often observed and cooling of the mixture is, therefore, recommended. If the ingredients have a high vapor pressure, it is desirable to keep the reaction temperature below about 70° to 80°C. Once the materials have been well mixed the complex is permitted to cool to room temperature. No special storage conditions are required although it is preferred that the complex be kept in a capped vessel in a cool, dark location. Advantageously, the complexes of the invention can be prepared in the absence of organic solvents that would later have to be removed, although they could be prepared in solvent if so desired. Solvents used in the preparation of the complexes should, preferably, be ones that do not coordinate amine, for example, tetrahydrofuran or hexane.

Advantageously, the organoborane polyamine complexes of the invention are air stable. By "air stable" it is meant that when the complexes are stored in a capped vessel at room temperature (about 20° to 22°C) and under otherwise ambient conditions (i.e., not under a vacuum and not in an inert atmosphere), the complexes remain useful as polymerization initiators for at least about two weeks, although the complexes may be readily stored under these conditions for many months.

By "air stable" it is also meant that the complexes are not pyrophoric. (When a few drops of the complex are placed on a paper towel under ambient conditions, the paper towel does not ignite.) The air stability of the complex is enhanced when the complex is a crystalline material. However, the complexes of the invention are air stable for at least six months even when they are liquids. Liquid complexes are easier to handle and mix than are crystalline complexes.

The organoborane polyamine complex is employed in an effective amount, which is an amount large enough to permit polymerization to readily occur to obtain a polymer (preferably, an acrylic polymer) of high enough molecular weight for the desired end use. If the amount of organoborane polyamine complex is too low, then the polymerization may be incomplete or, in the case of adhesives, the resulting composition may have poor adhesion. On the other hand, if the amount of organoborane polyamine complex is too high, then the polymerization may proceed too rapidly to allow for effective mixing and use of the resulting composition. Large amounts of complex could also lead to the generation of large volumes of borane, which, in the case of an adhesive, could weaken the bondline. The useful rate of polymerization will depend in part on the method of applying the composition to a substrate. Thus, a faster rate of polymerization may be accomodated by using a high speed automated industrial adhesive applicator rather than by applying the composition with a hand applicator or by manually mixing the composition.

Within these parameters, an effective amount of the organoborane polyamine complex is an amount that preferably provides about 0.03 to 1.5 weight % boron, based on the total weight of the adhesive composition, more preferably about 0.1 to 0.3 weight % boron.

The weight % of boron in a composition is equal to the following:

$$\frac{(\text{weight of complex in the composition}) \times (\text{weight \% of boron in the complex})}{(\text{Total weight of composition})}$$

The organoborane polyamine complexes of the invention are especially useful as polymerization initiators, in particular, for initiating the polymerization of acrylic monomers. In such cases, the organoborane polyamine complexes form one component of a polymerization initiator system that comprises and, more preferably, consists essentially of an effective amount of the organoborane polyamine complex and an effective amount of a compound that is reactive with amine for liberating organoborane so as to initiate polymerization.

The organoborane liberator evolves organoborane by reacting with the polyamine, thereby removing the organoborane from chemical attachment with the polyamine. A wide variety of materials may be used to provide the organoborane liberator. Desirable organoborane liberators are those materials that can readily form reaction products with amines at or below (and, more preferably, at) room temperature (about 20° to 22°C) so as to provide a composition such as an adhesive that can be easily used and cured under

ambient conditions. General classes of such compounds include isocyanate, acid chloride, sulfonyl chloride, aldehyde, and the like. Particular examples of compounds falling within these general classes include toluene diisocyanate, benzaldehyde, and methacryloyl chloride.

The organoborane liberator is employed in an effective amount; that is, an amount effective to promote polymerization by liberating organoborane from the complex but without materially adversely affecting the properties of the ultimate polymerized composition. Larger amounts of organoborane liberator may permit the polymerization to proceed too quickly and, in the case of adhesives, the resulting materials may demonstrate inadequate adhesion to low energy surfaces. Undesirable side reactions that adversely affect the performance properties of the polymerized composition, or an undesirably high level of extractables in the polymerized composition may also result from using large amounts of organoborane liberator. On the other hand, an excess of certain organoborane liberators may promote adhesion to higher energy surfaces. If small amounts of organoborane liberator are employed, the rate of polymerization may be too slow and the monomers that are being polymerized may not adequately increase in molecular weight. However, a reduced amount of organoborane liberator may be helpful in slowing the rate of polymerization if it is otherwise too fast.

Within these parameters, the organoborane liberator may be provided in an amount wherein the number of equivalents of amine reactive groups is as

much as twice stoichiometric with the number of amine groups in the organoborane polyamine complex. The number of amine groups includes both primary and secondary amine groups in the polyamine. However, it is much more preferred that the number of equivalents of amine reactive groups be stoichiometric with the total number of amine groups in the organoborane polyamine complex.

Acids may also be used as the organoborane liberator. Any acid that can liberate the organoborane by salting the polyamine group may be employed. Useful acids include Lewis acids (e.g., $SnCl_4$, $TiCl_4$ and the like) and Bronsted acids such as those having the general formula R-COOH, where R is hydrogen, an alkenyl group of 1 to 8 and preferably 1 to 4 carbon atoms, or an aryl group of 6 to 10, preferably 6 to 8 carbon atoms. The alkenyl groups may comprise a straight chain or they may be branched. They may be saturated or unsaturated. The aryl groups may contain substituents such as alkyl, alkoxy or halogen moieties. Illustrative acids of this type include acrylic acid, methacrylic acid, acetic acid, benzoic acid, and p-methoxybenzoic acid. Other useful Bronsted acids include HCl, H_2SO_4, H_3PO_4 and the like. Acrylic acid and methacrylic acid are preferred.

Somewhat different formulating is preferred with acids which, preferably, are provided in an amount of about 100 to 350 mole % based on the number of equivalents of amine groups, present in the complex (including primary, secondary and tertiary amines), more preferably about 150 to 250 mole %.

The organoborane polyamine complex initiator systems of the invention are especially useful in polymerizing acrylic monomers, particularly for making polymerizable acrylic adhesives. By "acrylic monomer" is meant polymerizable monomers having one or more acrylic or substituted acrylic moieties, chemical groups or functionality; that is, groups having the general structure



wherein R is hydrogen or an organic radical and R' is an organic radical. Where R and R' are organic radicals, they may be the same or they may be different. Blends of acrylic monomers may also be used. The polymerizable acrylic monomer may be monofunctional, polyfunctional or a combination thereof.

The most useful monomers are monofunctional acrylate and methacrylate esters and substituted derivatives thereof such as hydroxy, amide, cyano, chloro, and silane derivatives as well as blends of substituted and unsubstituted monofunctional acrylate and methacrylate esters. Particularly preferred monomers include lower molecular weight methacrylate esters such as methyl methacrylate, ethyl methacrylate, methoxy ethyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, cyclohexyl methacrylate, tetrahydrofurfuryl methacrylate, and blends thereof.

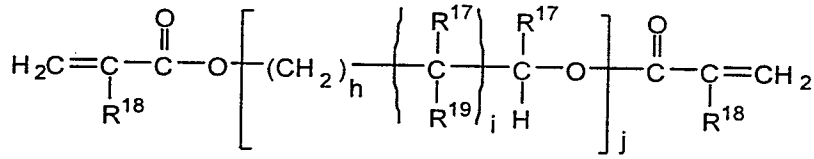
Both acrylate esters and higher molecular weight methacrylate esters are less preferred for use alone, but can be especially usefully employed as modifying monomers with predominating amounts of lower molecular

weight methacrylate esters so as to, for example, enhance the softness or flexibility of the ultimate composition. Examples of such acrylate esters and higher molecular weight methacrylate esters include methyl acrylate, ethyl acrylate, isobornyl methacrylate, hydroxypropyl acrylate, butyl acrylate, n-octyl acrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, decylmethacrylate, dodecyl methacrylate, tert-butyl methacrylate, acrylamide, N-methyl acrylamide, diacetone acrylamide, N-tert-butyl acrylamide, N-tert-octyl acrylamide, N-butoxyacrylamide, gamma-methacryloxypropyl trimethoxysilane, 2-cyanoethyl acrylate, 3-cyanopropyl acrylate, tetrahydrofurfuryl chloroacrylate, glycidyl acrylate, glycidyl methacrylate, and the like. Dimethylaminoethyl acrylate and dimethylamino methacrylate may also be used as modifying agents although additional organoborane liberator may be required due to the extra amine groups.

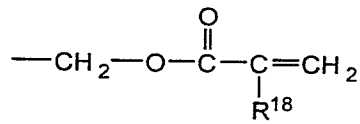
Particularly preferred are blends of any of the lower molecular weight alkyl methacrylate esters described above with alkyl acrylates having 4 to 10 carbon atoms in the alkyl group, such as blends of methyl methacrylate and butylacrylate. Polymerizable compositions of this type may broadly comprise, based on the total weight of the composition, about 2 to 40 wt. % of the alkyl acrylate and, correspondingly, about 60 to 98 wt. % of the alkyl methacrylate.

Another class of polymerizable monomers that are especially useful as modifiers, such as for improving the creep resistance or temperature resistance of the

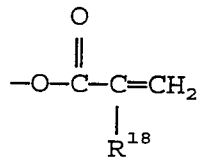
ultimate composition, corresponds to the general formula:



R^{17} may be selected from the group consisting of hydrogen methyl, ethyl, $-CH_2OH$, and



R^{18} may be selected from the group consisting of chlorine, methyl and ethyl. R^{19} may be selected from the group consisting of hydrogen, hydroxy, and

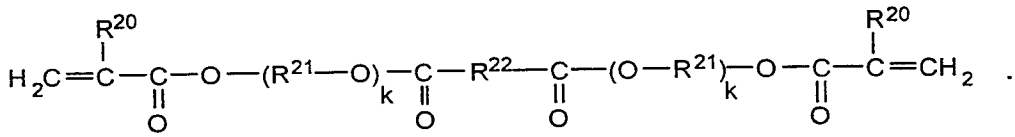


The value of h is an integer greater than or equal to 1, more preferably, from 1 to about 8, and most preferably from 1 to 4. The integral value of i is greater than or equal to 1, more preferably, from 1 to about 20. The value of j is 0 or 1.

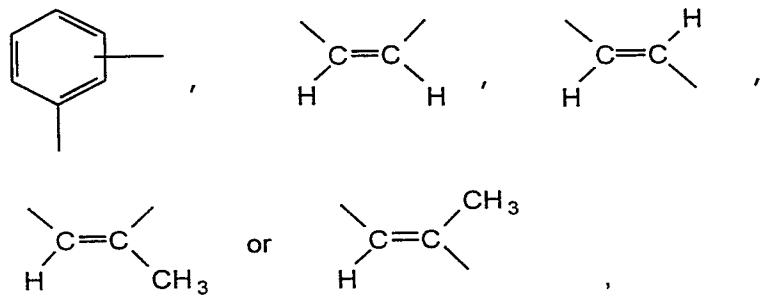
Other acrylic monomers useful with the polymerization initiator systems, especially as modifying monomers, include ethylene glycol dimethacrylate, ethylene glycol diacrylate, polyethylene glycol diacrylate, tetraethylene glycol dimethacrylate, diglycerol diacrylate, diethylene glycol dimethacrylate, pentaerythritol triacrylate,

trimethylolpropane trimethacrylate, as well as other polyether diacrylates and dimethacrylates.

Other polymerizable monomers that are useful in the invention, particularly as modifying monomers, have the general formula:



R^{20} may be hydrogen, chlorine, methyl or ethyl; R^{21} may be an alkylene group with 2 to 6 carbon atoms; and R^{22} is $(CH_2)_1$ in which 1 is an integer of 0 to 8, or one of the following:

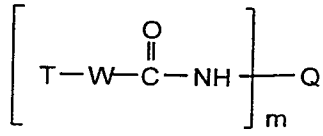


the phenyl group being substitutable at any one of the ortho, meta or para positions. The value of d is an integer of 1 to 4.

Typical monomers of this class include dimethacrylate of bis(ethylene glycol) adipate, dimethacrylate of bis(ethylene glycol) maleate, dimethacrylate of bis(ethylene glycol) phthalate, dimethacrylate of bis(tetraethylene glycol) phthalate, dimethacrylate of bis(tetraethylene glycol) sebacate, dimethacrylates of bis(tetraethylene glycol) maleate,

and the diacrylates and chloroacrylates corresponding to the dimethacrylates, and the like.

Also useful as modifying agents are monomers that are isocyanate-hydroxyacrylate or isocyanate-aminoacrylate reaction products. These may be characterized as acrylate terminated polyurethanes and polyureides or polyureas. Such monomers have the following general formula:

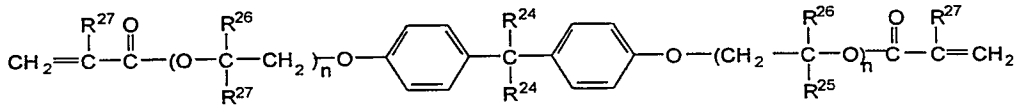


where W is selected from the group consisting of —O— and  . R^{23} is selected from the group consisting of hydrogen and lower alkyl groups (e.g., 1 to 7 carbon atoms). T is the organic residue of an active hydrogen-containing acrylic ester, the active hydrogen having been removed and the ester being hydroxy or amino substituted on the alkyl portion thereof (including the methyl, ethyl and chlorine homologs). The integral value of m is from 1 to 6. Q is a mono- or polyvalent organic radical selected from the group consisting of alkyl, alkylene, alkenyl, cycloalkyl, cycloalkylene, aryl, aralkyl, alkaryl, poly(oxyalkylene), poly(carboalkoxyalkylene), and heterocyclic radicals, both substituted and unsubstituted.

Typical monomers of this class include the reaction product of mono- or polyisocyanates, for example, toluene diisocyanate, with an acrylate ester containing a hydroxy or an amino group in the non-

acrylate portion thereof, for example, hydroxyethyl methacrylate.

Still another class of modifying monomers useful in the present invention are the mono- and polyacrylate and methacrylate esters of bisphenol type compounds. These monomers may be described by the following formula:



where R^{24} is methyl, ethyl, carboxyalkyl or hydrogen; R^{25} is hydrogen, methyl or ethyl; R^{26} is hydrogen, methyl or hydroxyl; R^{27} is hydrogen, chlorine, methyl or ethyl; and g is an integer having a value of 0 to 8. Representative monomers of the above-described class include dimethacrylate and diacrylate esters of 4,4'-bis-hydroxyethoxy-bisphenol A, dimethacrylate and diacrylate esters of bisphenol A, etc.

The compositions may further comprise a variety of optional additives. One particularly useful additive is a thickener such as medium (about 100,000) molecular weight polymethyl methacrylate which may be incorporated in an amount of about 10 to 40 weight %, based on the total weight of the composition. Thickeners may be employed to increase the viscosity of the composition to a more easily applied viscous syrup-like consistency.

Another particularly useful additive is an elastomeric material. These materials can improve the fracture toughness of compositions made therewith which

can be beneficial when, for example, bonding stiff, high yield strength materials such as metal substrates that do not mechanically absorb energy as easily as other materials, such as flexible polymeric substrates. Such additives can be incorporated in an amount of about 5% to 35% by weight, based on the total weight of the composition.

Useful elastomeric modifiers include chlorinated or chlorosulphonated polyethylenes such as HYPALON 30 (commercially available from E. I. duPont de Nemours and Co., Wilmington DE). Also useful, and even more preferred, are certain graft copolymer resins such as particles that comprise rubber or rubber-like cores or networks that are surrounded by relatively hard shells, these materials often being referred to as "core-shell" polymers. Most preferred are the acrylonitrile-butadiene-styrene graft copolymers.

In addition to improving the fracture toughness of the composition, core-shell polymers can also impart enhanced spreading and flow properties to the uncured composition. These enhanced properties may be manifested by a reduced tendency for the composition to leave an undesirable "string" upon dispensing from a syringe-type applicator, or sag or slump after having been applied to a vertical surface. Use of more than about 20% of a core-shell polymer additive is desirable for achieving improved sag-slump resistance.

Another useful adjuvant is a crosslinking agent. Crosslinking agents can be used to enhance the solvent resistance of the adhesive bond, although certain compositions of the invention have good solvent

resistance even in the absence of externally added crosslinking agents. Typically employed in an amount of about 0.2 to 10 weight % based on the total weight of the composition, useful crosslinkers include the various diacrylates referred to above as possible acrylic modifying monomers as well as other materials. Particular examples of suitable crosslinking agents include ethylene glycol dimethacrylate, ethylene glycol diacrylate, triethyleneglycol dimethacrylate, diethylene glycol bismethacryloxy carbonate, polyethylene glycol diacrylate, tetraethylene glycol dimethacrylate, diglycerol diacrylate, diethylene glycol dimethacrylate, pentaerythritol triacrylate, trimethylolpropane trimethacrylate, as well as other polyether diacrylates and dimethacrylates.

Peroxides may be optionally included (typically in an amount of about 2 % by weight or less, based on the total weight of the composition), for example, to adjust the speed at which the compositions polymerize or to complete the polymerization.

Small amounts of inhibitors such as hydroquinone may be used, for example, to prevent or reduce degradation of the acrylic monomers during storage. Inhibitors may be added in an amount that does not materially reduce the rate of polymerization or the ultimate properties of an adhesive or other composition made therewith, typically about 100 - 10,000 ppm based on the weight of the polymerizable monomers.

Other possible additives include non-reactive colorants, fillers (e.g., carbon black), etc.

The various optional additives are employed in an amount that does not significantly adversely affect the polymerization process or the desired properties of compositions made therewith.

Polymerizable acrylic compositions according to the invention may be used in a wide variety of ways, including as sealants, coatings, and injection molding resins. They may also be used as matrix resins in conjunction with glass and metal fiber mats such as in resin transfer molding operations. They may further be used as encapsulants and potting compounds such as in the manufacture of electrical components, printed circuit boards and the like. Quite desirably, they provide polymerizable acrylic adhesive compositions that can bond a diverse myriad of substrates, including polymers, wood, ceramics, concrete, and primed metals.

Polymerizable acrylic compositions of the invention are especially useful for adhesively bonding low surface energy plastic or polymeric substrates that historically have been very difficult to bond without using complicated surface preparation techniques, priming, etc. By low surface energy substrates is meant materials that have a surface energy of less than 45 mJ/m^2, more typically less than 40 mJ/m^2 or less than 35 mJ/m^2. Included among such materials are polyethylene, polypropylene, acrylonitrile-butadiene-styrene, polyamide, and fluorinated polymers such as polytetrafluoroethylene (TEFLON) which has a surface energy of less than 20 mJ/m^2. (The expression "surface energy" is often used synonymously with "critical wetting tension" by others.) Other polymers of

somewhat higher surface energy that may be usefully bonded with the compositions of the invention include polycarbonate, polymethylmethacrylate, and polyvinylchloride.

The polymerizable compositions of the invention can be easily used as two-part adhesives. The components of the polymerizable composition are blended as would normally be done when working with such materials. The organoborane liberator of the polymerization initiator system is usually included in this blend so as to separate it from the organoborane polyamine complex, thus providing one part of the two-part composition. The organoborane polyamine complex of the polymerization initiator system provides the second part of the composition and is added to the first part shortly before it is desired to use the composition. The complex may be added to the first part directly or it may be predissolved in an appropriate carrier such as a small amount of methyl methacrylate.

While a primary amine nitrogen atom to boron atom ratio of about 1:1 in the organoborane polyamine complex is preferred, it is desirable to store such complexes apart from the monomers to inhibit premature polymerization of the monomers. Complexes in which the primary amine nitrogen atom to boron atom ratio is greater than 1:1 may be sufficiently stable that they can be blended with acrylic monomer in useful proportions. However, in such situations, the presence of additional non-polymerizing reactants (e.g., the

organoborane liberator) may result in other, undesirable affects.

For a two-part adhesive such as those of the invention to be most easily used in commercial and industrial environments, the ratio at which the two parts are combined should be a convenient whole number. This facilitates application of the adhesive with conventional, commercially available dispensers. Such dispensers are shown in U.S. Patent Nos. 4,538,920 and 5,082,147 and are available from Conprotec, Inc. (Salem NH) under the tradename "Mixpac." Typically, these dispensers use a pair of tubular receptacles arranged side-by-side with each tube being intended to receive one of the two parts of the adhesive. Two plungers, one for each tube, are simultaneously advanced (e.g., manually or by a hand-actuated ratcheting mechanism) to evacuate the contents of the tubes into a common, hollow, elongated mixing chamber that may also contain a static mixer to facilitate blending of the two parts. The blended adhesive is extruded from the mixing chamber onto a substrate. Once the tubes have been emptied, they can be replaced with fresh tubes and the application process continued.

The ratio at which the two parts of the adhesive are combined is controlled by the diameter of the tubes. (Each plunger is sized to be received within a tube of fixed diameter, and the plungers are advanced into the tubes at the same speed.) A single dispenser is often intended for use with a variety of different two-part adhesives and the plungers are sized to deliver the two parts of the adhesive at a convenient

mix ratio. Some common mix ratios are 1:1, 2:1, 4:1 and 10:1.

If the two parts of the adhesive are combined in an odd mix ratio (e.g. 100:3.5), then the ultimate user would probably manually weigh the two parts of the adhesive. Thus, for best commercial and industrial utility and for ease of use with currently available dispensing equipment, the two parts of the adhesive should be capable of being combined in a common, whole number mix ratio such as 10:1 or less, more preferably 4:1, 3:1, 2:1 or 1:1.

Adhesive compositions of the invention are uniquely suited for use with conventional, commercially available dispensing equipment for two-part adhesives. The organoborane polyamine complexes of the invention have a relatively high molecular weight (as compared to other known organoborane amine complexes). Consequently, the complex can comprise essentially all of the second part of the adhesive while still providing an effective amount of organoborane in a useful whole number mix ratio of 10:1 or less.

Once the two parts have been combined, the composition should be used quickly, as the useful pot life may be short depending upon the acrylic monomer mix, the amount of complex, and the temperature at which the bonding is to be performed.

The polymerizable composition is applied to one or both substrates and then the substrates are joined together with pressure to force excess composition out of the bond line. This also has the advantage of displacing composition that has been exposed to air and

that may have begun to oxidize. In general, the bonds should be made shortly after the composition has been applied, preferably within about 10 minutes. The typical bond line thickness is about 0.1 to 0.3 mm. The bonding process can easily be carried out at room temperature and to improve the degree of polymerization it is desirable to keep the temperature below about 40°C, preferably below 30°C, and most preferably below about 25°C.

The bonds will cure to a reasonable green strength to permit handling of the bonded components within about 2 to 3 hours. Full strength will be reached in about 24 hours under ambient conditions; post-curing with heat (typically about 80°C) may be used if desired.

When bonding fluoroplastics, it is advantageous to cool the first part of the two-part composition to about 0 to 5°C before adding the organoborane polyamine complex. The bond should be made as soon after the composition has been applied as practical; performing the bonding operation at less than room temperature is also helpful.

The invention will be more fully appreciated with reference to the following nonlimiting examples in which (unless noted otherwise) all weights are given as weight percents (weight %), based on the total weight of the composition which is 100 weight%.

Examples that were subsequently evaluated to measure the lap shear strength of the adhesive bonds were tested as described below.

Lap Shear Strength Test Method

The test specimens used were similar to that described in ASTM D-1002 except that the specimens were generated using finger panels of nominal dimensions 1 in. x 4 in. x 1/8 in. thick (2.5 cm x 10.2 cm x 0.3 cm thick). 0.5 in. (1.3 cm) wide red lithographers tape was applied to the end of one of the adherends in order to help fixture the bond and also to aid in making the lap region to be 0.5 in. (1.3 cm). Short pieces of 6 mil (0.15 mm) diameter piano wire were cut for use as spacers to control the thickness of the adhesive bondline.

The adhesive was prepared by weighing the monomer mixture into a vial that was capable of being sealed with a poly cap. Organoborane polyamine initiator complex was then added, blended with the monomer mixture using a wooden stick, and the vial was sealed with the poly cap. In general, the addition of organoborane polyamine amine initiator complex to the monomer mixture caused the mixture to slightly exotherm and, in some cases, turn yellow. A dab of the mixed adhesive was applied to each adherend and spread to make sure that a 1 in. x 0.5 in. (2.5 cm x 1.3 cm) area was covered at the end of each adherend. Two pieces of piano wire were placed into the adhesive on one adherend and the bond was closed and fixtured with the lithographers tape. The bond was further fixtured with two binder clips and allowed to cure at room temperature for 48 hours at which time the binder clips and tape were removed.

Lap shear testing was done with three types of adherends: mechanical grade TEFLON, high density polyethylene, and polypropylene, as available from Precision Punch and Plastic Co. (Minneapolis, MN). Three adhesive bonds were made with each adherend and each adhesive combination. For each adhesive, the TEFLON was bonded first, then the high density polyethylene, and then the polypropylene. After curing, the bonds were tested to failure using a Tensile Testing Machine. The crosshead speed was 0.1 in./minute (2.5 mm/min.) and the tests were carried out at room temperature. Bonds were visually inspected after being loaded to failure to determine the failure mode. Failure of the adherends is the most preferred although cohesive failure of the composition evidences a useful formulation.

Failure modes are reported in the examples based on a series of coded abbreviations which may be interpreted as follows:

Abbreviation	Failure Mode
a	Good filet adhesion
b	One or more bonds stretched to yield of the adherend without failure
c	Mixed mode failure
d	Failure of the adherend
e	Cohesive failure within the adhesive
f	Adhesion failure of the adhesive
g	Incomplete wetting; puddling of the adhesive

Example 1

Example 1 describes the preparation of a series of polyamines according to the invention and based on the reaction product of various diprimary amine-terminated materials (i.e., diamines) and various diacrylates. More specifically, the diamine and the diacrylate were mixed in a jar. The jar was placed on a hot plate and stirred occasionaly while heating to a temperature of about 70°C until a clear, viscous liquid resulted. The polyamines that were synthesized are shown below in Table 1 which also shows the benefit of combining diacrylates with acrylates to form a polyamine with an intermediate equivalent weight and a more useful viscosity.

Table 1

Polyamine	Diamine	Approximate Primary Amine Equivalent Weight	Amount of Diamine (g)	Acrylate or Diacrylate	Approximate Acrylate/Diacrylate Equivalent Weight	Amount of Acrylate or Diacrylate (g)	Comments
PA-A	Polypropylene oxide diamine (Jeffamine D400)	215	141.0	Urethane-diacrylate oligomer (Uvithane 783) + Polyethylene glycol diacrylate (Photomer 4050)	533 155	75.0 25.0	Clear liquid about 20,000 cP
PA-B	Polypropylene oxide diamine (Jeffamine D400)	215	139.0	Urethane-diacrylate oligomer (Uvithane 783) + Tetrahydrofurfuryl acrylate	533 156	75 25.0	Clear liquid about 20,000 cP
PA-C	Polypropylene oxide diamine (Jeffamine D400) + Polypropylene oxide diamine (Jeffamine D2000)	215 1028	52.0 78.0	Urethane-diacrylate oligomer (Photomer 6210)	700	100.0	Clear liquid about 20,000 cP
PA-D	Polypropylene oxide diamine (Jeffamine D2000)	1028	154.0	Urethane-diacrylate oligomer (Photomer 6210)	700	50.0	Clear liquid about 15,000 cP

The various "Jeffamines" used to prepare the polyamines shown in Table 1 are commercially available from Huntsman Chemical Company. Uvithane 783 is commercially available from Morton International. Photomer 4050 and Photomer 6210 are commercially available from Henkel GmbH.

The polyamines described in Table 1 were then reacted with triethylborane according to the method described hereafter so as to form organoborane polyamine complexes according to the invention and as shown in Table 2 below.

More specifically, the complexes were prepared using glassware that had been washed and fired at 1000°F (538°C) or fired by means of a Bunsen burner until the glassware glowed orange. A polyethylene glove bag was set up and flushed with nitrogen. (In some cases, the synthesis was carried out in a glove box which had been inerted with nitrogen.) The glove bag or glove box contained a pressure equalizing dropping funnel, an electric balance, a flask with appropriate stoppers, and a stand.

The polyamine was degassed by freeze-thaw cycles under vacuum and was then weighed into the flask. The organoborane was weighed into the pressure equalizing dropping funnel and then added dropwise to the polyamine with stirring and cooling. A mild exotherm was observed and the addition of the organoborane was moderated to control the exotherm. In some cases, fuming occurred and the addition of the organoborane was slowed until the fuming had subsided. Once all of the organoborane had been added, the flask was allowed

to equilibrate to room temperature. The resulting complex was poured from the flask into a bottle and sealed.

Table 2

Complex	Polyamine	Calculated Primary Amine Equivalent Weight	Amount of Polyamine (g)	Amount of Triethyl Borane (g)	Ratio of Primary Amine Nitrogen Atoms to Boron Atoms	Comments
A	PA-A	680	241	31.5	1.1:1	Clear liquid
B	PA-B	691	239	17.4	1.9:1	Clear liquid
C	PA-C	1315	230	15.0	1.14:1	Clear liquid
D	PA-D	2629	204	15.3	0.5:1	Clear liquid

Example 2

A series of two-part acrylic adhesives was prepared using the organoborane polyamine complexes from Table 1 and a mixture of acrylic monomers comprising 78 g of methyl methacrylate, 56 g of n-butyl acrylate, 60 g of medium molecular weight poly(methyl methacrylate) (101,000 molecular weight poly(methylmethacrylate-co-ethyl acrylate) with less than 5% ethyl acrylate from Aldrich Chemical Co.), and 6 g of methacrylic acid. These monomers were weighed into a 1 quart brown bottle that was sealed and placed in a Launder-o-meter set at 55°C overnight. A light yellow to white, clear, moderately viscous solution resulted. This is referred to herein as Monomer Mixture A.

Monomer Mixture A formed one part of the two-part acrylic adhesive while the organoborane polyamine complex formed the entirety of the second part. The adhesives were formulated such that the mix ratios of the two parts were an industrially useful 4:1 or 2:1.

The lap shear strength of bonded composites prepared with these adhesives was tested using the method described above and with the results shown below in Table 3.

Table 3

Complex	Mix Ratio (Monomer Mixture A: Complex)	Lap Shear to TEFLON (psi)	Lap Shear to Polyethylene (psi)	Lap Shear to Polypropylene (psi)	Mode of Failure
A	4:1	319	550	400	e (all)
B	4:1	155	356	320	e (all)
C	2:1	47	300	218	e (others) f (Teflon)
D	2:1	141	410	410	e (all)

Table 3 shows that good adhesive bonds to low surface energy polymeric substrates are possible using the complexes and adhesives of the invention, as evidenced by the largely cohesive failure modes. While the performance of the adhesive employing complex A was particularly good, at least equal results could be obtained for the other complexes by appropriate optimization of Monomer Mixture A for those complexes.

Example 3

Example 3 describes the preparation of a series of polyamines according to the invention and based on the reaction product of various diprimary-amine terminated materials (i.e., diamines) and various diepoxides as shown below in Table 4. The polyamines were produced by mixing the diepoxide and the diamine neat and at room temperature using a stoichiometry of 2.1 moles of diprimary amine-terminated material per mole of diepoxide so as to provide a substantially linear material terminated by primary amine.

Table 4

Polyamine	Diamine	Approximate Primary Amine Equivalent Weight	Amount of Polyamine (g)	Epoxide	Approximate Epoxide Equivalent Weight	Amount of Epoxide (g)
PA-E	Polypropylene oxide diamine (Jeffamine D400)	215	30.9	Diglycidly ether of bisphenol A (Epon 828)	190	12.1
PA-F	Poly(ethylene co-polypropylene oxide) diamine (Jeffamine ED600)	318	34.0	Diglycidly ether of bisphenol A (Epon 828)	190	9.6
PA-G	1,5 diamino-2-methylpentane (Dytek A)	58	12.1	Polyglycol diepoxide DER 732	320	32.0

The "Jeffamine" materials are commercially available from Huntsman Chemical Company. "Dytek A" is commerciallly available from E.I. duPont de Nemours and Co. "Epon 828" is commercially available from Shell Chemical Company. "DER 732" is commercially available from Dow Chemical Company.

Organoborane polyamine complexes according to the invention were prepared using the polyamines described in Table 4 and triethylborane, employing the procedure described in conjunction with example 1, and as shown below in Table 5.

Table 5

Complex	Polyamine	Calculated Primary Amine Equivalent Weight	Amount of Polyamine (g)	Amount of Triethyl Borane (g)	Ratio of Primary Organoborane Nitrogen Atoms to Boron Atoms	Viscosity (cP)	Comments
E	PA-E	538	43.0	6.9	1.1:1	15,000	Clear liquid
F	PA-F	773	43.5	5.5	1:1	20,000	Clear liquid
G	PA-G	406	44.0	10.8	1:1	20,000	Clear liquid

Example 5

A series of two-part acrylic adhesives was prepared using the organoborane polyamine complexes from Table 5 and Monomer Mixture A (described in conjunction with example 2). Some of the adhesives were based on a second monomer mixture (referred to herein as Monomer Mixture B) which was prepared like Monomer Mixture A but comprised 39 parts methyl methacrylate, 28 parts butyl n-acrylate, 6 parts methacrylic acid, and 17.5 parts of the same medium molecular weight poly(methylmethacrylate) used in Monomer Mixture A.

The Monomer Mixture (either A or B) formed one part of the two-part acrylic adhesive while the organoborane polyamine complex formed the entirety of the second part. The lap shear strength of bonded composites using these adhesives was tested as described above and with the results shown below in Table 6.

Table 6

Complex Designation	Monomer Mixture	Ratio of Monomer Mixture to Complex	Lap Shear to TEFLON (psi)	Failure Mode	Lap Shear to Polyethylene (psi)	Failure Mode	Lap Shear to Polypropylene (psi)	Failure Mode
E	A	3.1:1	147	f	300	e	400	e
E	B	5:1	310	e	435	e	639	e,d
F	A	5:1	234	e	168	e	332	e
F	B	10:3	287	e	259	e	419	e
G	A	9:1	311	e	643	e	600	d
G	B	10:3	153	f	438	e	471	e

Table 6 demonstrates that useful two-part structural acrylic adhesives according to the invention can be prepared using polymerization initiator systems that include organoborane polyamine complexes wherein the polyamine is the reaction product of diprimary amine-terminated material and diepoxide. The combination of complex G with Monomer Mixture A provided particularly superior results. Although some odd mix ratios were employed, optimizing the monomer mixture formula would be expected to yield good adhesives having even mix ratos.

Example 6

Example 6 describes the use of an organoborane polyamine complex according to the invention in which the polyamine is the reaction product of diprimary amine-terminated material and a dimer acid. More specifically, a complex having a 1:1 primary amine nitrogen atom to boron atom ratio and 2.26 weight % boron was generated by reacting 8.04 g of triethylborane with 31.15 g of VERSAMID 125 (commercially available from Henkel GmbH).

As shown below in Table 8, two-part acrylic adhesives were prepared by combining varying amounts of the complex of this example with 5 g. of Monomer Mixtures C, D and E (described below and in Table 7) using the techniques described above in conjunction with example 2. The resulting adhesives were tested for lap shear strength using the procedures described above and with the results shown below in Table 8.

Monomer Mixtures C, D and E were each based on methyl methacrylate, n-butyl acrylate, methacrylic acid, and the same medium molecular weight poly(methyl methacrylate) (PMMA) used in Monomer Mixture A. The amount of methacrylic acid in the different monomer mixtures was varied so as to provide a sufficient amount to liberate the organoborane to initiate polymerization but without materially adversely affecting adhesive performance due to the presence of a high surface tension material that could inhibit surface wetting by the adhesive.

Table 7

Monomer Mixture	Methyl Methacrylate (g)	n-Butyl Acrylate (g)	Methacrylic Acid (g)	PMMA (g)
C	40.54	29.16	0.30	30.0
D	40.26	28.97	0.77	30.0
E	36.06	25.94	8.00	30.0

Table 8

Amount of Complex (g)	Monomer Mixture	Weight% Boron in the Adhesive Compos-ition	Lap Shear on TEFLON (psi)	Failure Mode	Lap Shear on Polyeth-ylene (psi)	Failure Mode	Lap Shear on Polypro pylene (psi)	Failure Mode
0.031	C	0.14	0	g	2.7	g	6	g
0.10	D	0.046	10.7	f	385	a,e	280	c,e,g
0.23	E	0.099	342	b,e	400	e	484	a,e
0.51	E	0.21	236	a,c	406	c,e,g	414	d,e,a

The organoborane polyamine complexes of the invention provide adhesives that give excellent adhesion to low energy polymeric surfaces when the boron content in the adhesive exceeds 0.03 % by weight. The last entry in Table 8 demonstrates that the

complexes of the invention can form one part of a two-part acrylic adhesive in which the two parts are combined in an industrially useful 10:1 mix ratio.

Example 7

In example 7, two organoborane polyamine complexes based on triethylborane and a polyamine comprising the reaction product of "Epon 828" (a diglycidyl ether of bisphenol A, commercially available from Shell Chemical Company), and either H221 (a diethylene glycol bis-propylamine commercially available from Union Carbide Company) or 1,3-propane diamine were prepared.

The polyamines were produced by weighing the diamine into a bottle and heating to 50°C with stirring. The "Epon 828" was added slowly, with stirring, allowed to react at 50°C for one hour, and then cooled. The polyamines are shown below in Table 9.

Table 9

Polyamine	Diamine	Approximate Primary Amine Equivalent Weight	Amount of Polyamine (g)	Epoxide	Approximate Epoxide Equivalent Weight	Amount of Epoxide (g)
PA-H	H221	380	36.9	Epon 828	190	30.0
PA-I	1,3-propane diamine	240	12.5	Epon 828	190	30.0

Organoborane polyamine complexes were then prepared. More specifically and as shown below in Table 10, the complexes were made in a dry box. The polyamine was degassed by means of freeze-thaw cycles using liquid nitrogen and vacuum. 4 oz. jars and caps which had been modified by drilling a hole through them

were placed in the dry box. In addition, triethylborane, a magnetic stirrer, a balance, and a pressure equalizing dropping funnel were placed in the dry box. The dry box was inerted with nitrogen. Polyamine was weighed into the jars and each jar was closed with a cap that had a hole drilled through it. The triethyl borane was weighed into the dropping funnel which was then fitted into the hole in the cap. The polyamine was cooled with an ice/water bath and the triethyl borane was slowly dripped into the polyamine with stirring. The addition proceeded at a rate that minimized fuming and the exotherm. When all of the triethyl borane had been added the jar was sealed with a regular cap and stirred with cooling for 1/2 hour. The jar was left at room temperature in the dry box overnight after which it was removed.

Table 10

Complex	Triethyl-borane (g)	Equivalents of Borane	Polyamine		Ratio Primary Amine Nitrogen Atoms to Boron Atoms	Weight % Boron	Total Amine Equivalent Weight
			Designation	Amount (g)			
H	7.73	0.079	PA-H	30.0	1:1	2.26	250.3
I	12.25	0.125	PA-I	30.0	1:1	3.2	177.5

Example 8

In example 8, two organoborane polyamine complexes based on triethyl borane and a polyamine comprising the reaction product of diethylene glycol bis-propylamine (H221 from Union Carbide Company) and 1,6-hexanediol diacrylate were prepared.

More specifically, the polyamine was prepared by placing 100 g. H221 in a bottle and heating with stirring to 50°C in a water bath. 48.9 grams of 1,6 hexanediol diacrylate were then added slowly to the H221 with stirring. The reaction was allowed to proceed at 50°C for 1 hour at which time it was allowed to cool to room temperature. A clear, moderately viscous liquid resulted.

The complexes were then generated as shown below in Table 11 using the techniques described in conjunction with example 7.

Table 11

Complex	Triethyl-borane (g)	Equivalents of Borane	Poly-amine (g)	Calculated Equi-valents of Primary Amine	Ratio Primary Amine Nitrogen Atoms to Boron Atoms	Weight % Boron	Total Amine Equi-valent Weight
J	17.94	0.183	30.0	0.096	0.5:1	4.12	261.8
K	9.42	0.096	30.0	0.096	1:1	2.63	215.2

Example 9

A series of adhesive compositions comprising 5 g. Monomer Mixtures F, G and H (described below and in Table 12), and varying amounts of organoborane polyamine complexes A, D, H, I, J, and K were then prepared. Each monomer mixture was based on methyl methacrylate, n-butyl acrylate, methacrylic acid, and the same medium molecular weight poly(methylmethacrylate) (PMMA) used to prepare Monomer Mixture A. The amount of methacrylic acid in the different monomer mixtures was varied so as to provide a sufficient amount to liberate the organoborane to initiate polymerization but without materially

adversely affecting adhesive performance due to the presence of a high surface tension material that could inhibit surface wetting by the adhesive. The monomer mixtures were generated by mixing all of the ingredients in a bottle and then stirring with the aid of a roller mill and mild heat until all of the ingredients had dissolved.

Table 12

Monomer Mixture	Methyl Methacrylate (g)	n-Butyl Acrylate (g)	Methacrylic Acid (g)	PMMA (g)
F	39.00	28.00	3.0	30.0
G	37.80	27.20	5.0	30.0
H	36.63	6.35	7.0	30.0

The adhesive compositions were then tested for lap shear strength using the technique described above and with the results shown below in Table 13.

Table 13

Monomer Mixture	Complex	Amount of Complex (g)	Weight % Boron in Mix	Lap Shear to TEFLON (psi)	Failure Mode	Lap Shear to Polyethylene (psi)	Failure Mode	Lap Shear to Polypropylene (psi)	Failure Mode
F	H	0.03	0.014	10	f	7	f	27	f
F	H	0.10	0.044	14	f	128	f	253	f
F	H	0.23	0.099	229	c	522	e	758	d
G	H	0.51	0.21	310	c,e	457	e	700	d
H	H	1.00	0.376	219	c,f	386	c,e	515	d,e
F	I	0.02	0.013	2	f	46	f	18	f
F	I	0.06	0.038	76	f	87	f	61	f
F	I	0.16	0.099	153	a,f	295	c	455	c
G	I	0.37	0.22	155	c,f	500	c	611	d,e
H	I	0.50	0.291	287	c,e	438	c	554	d,e
F	A	0.06	0.015	0	f	0	f	14	f
F	A	0.16	0.039	0	f	9	f	16	f
F	A	0.40	0.094	128	c,f	339	c	721	d
G	A	0.95	0.203	307	c,e	427	c,e	695	d,e
H	A	1.25	0.254	305	e	467	c,e	720	d,e
F	D	0.21	0.015	0	f	0	f	0	f
F	D	0.55	0.038	25	f	85	c	135	c
F	D	1.40	0.084	143	c,f	320	e	461	e
G	D	3.20	0.15	237	e	461	e	459	e
H	D	5.00	0.19	260	e	585	e	419	e
F	H	0.02	0.016	14	f	10	f	15	f
F	H	0.05	0.041	194	a,f	176	f	625	d
F	H	0.12	0.096	368	b,c	366	e	701	d
G	H	0.30	0.233	336	b,e	398	e	851	d
H	H	0.50	0.375	292	e	423	e	594	e
F	J	0.03	0.016	9	f	3	f	8	f
F	J	0.08	0.041	29	f	170	f	141	f
F	J	0.20	0.1	334	b,c	368	c	911	b,c,d
G	J	0.45	0.217	363	b	430	c,e	823	d
G	K	0.50	0.239	302	b,e	531	e	851	e

These data show that adhesion is affected by the amount of boron. Surprisingly, complex H was not pyrophoric and could be used to provide an adhesive that bonded low energy plastic surfaces even though its stoichiometry was such that 1/2 of the borane was complexed with secondary amine rather primary amine. Consequently, significantly larger amounts of borane can be included in the adhesive without adding large amounts of material which do not participate in the polymerization of the adhesive monomers.

Table 13 also shows that the complexes of the invention can provide adhesives in which the two parts are combined in industrially useful mix ratios of 1:1 to 10:1

Example 10

Example 10 describes the performance of a pair of known two-part acrylic adhesives, "DP-805" which is commercially available from the 3M Company (St. Paul, MN), and an adhesive that is intended to be based on U.S. Patent 4,536,546, example 5 but using currently available materials (referred to herein as adhesive X). The formulation of adhesive X is as follows:

Part A:

35.5 parts HYPALON 30 (from E.I. duPont de Nemours)

53.2 parts methyl methacrylate

9.8 parts methacrylic acid

1 part cumene hydroperoxide

Part B:

25 parts BLENDEX B467 (acrylonitrile-butadiene-styrene terpolymer from General Electric Specialty Chemicals, Parkersburg, WV)

75 parts methyl methacrylate

4.995 parts VANAX 808 (from Vanderbilt Chemical Co.)

0.005 part copper napthenate solution

Part A was generated by mixing the components until a viscous solution resulted. Part B was generated by first mixing the graft co-polymer and the methyl methacrylate until a stable bluish dispersion resulted. The VANAX 808 and copper napthenate were then added. Adhesive bonds were made and tested for lap shear strength as described above but with the exception that bonds were also made on 2024-T3 aluminum substrates according to the method described in ASTM D-1002. The results are shown below in Table 14.

Table 14

	DP-805	Adhesive X
Lap Shear on Aluminum (psi)	3288	3688
Lap Shear on TEFLON (psi)	26	17
Lap Shear on Polyethylene (psi)	18	12
Lap Shear on Polypropylene (psi)	2.7	16

Table 14 in combination with other data herein shows that two-part acrylic adhesive compositions according to the invention which include an effective amount of boron (as provided by the organoborane polyamine complexes of the invention) have excellent adhesion to low surface energy plastics whereas other known two-part acrylic adhesives do not. However, the known adhesives do provide good adhesion to aluminum

substrates. The known adhesives suffered cohesive failure with the aluminum substrates but failed adhesively with the polymeric substrates.

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

CLAIMS

The embodiments for which an exclusive property or privilege is claimed are defined as follows:

1. A complex comprising organoborane and polyamine, wherein the polyamine comprises the reaction product of a diprimary amine-terminated material and a material having at least two groups reactive with primary amine, wherein a majority of the terminal groups in the polyamine are primary amine.

2. A complex according to claim 1 wherein the organoborane has structure



wherein:

R^1 is an alkyl group having 1 to 10 carbon atoms; and

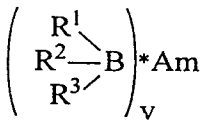
R^2 and R^3 are independently selected from alkyl groups having 1 to 10 carbon atoms and phenyl-containing groups.

3. A complex according to claim 1 wherein the diprimary amine-terminated material is selected from the group consisting of polyoxyalkylenediamine, alkyl diamine, aryl diamine, alkaryl diamine, and blends thereof.

4. A complex according to claim 1 wherein the material having at least two groups reactive with primary amine has the structure Y-R-Z, wherein Y and Z are moieties reactive with primary amine and are independently selected from the group consisting of carboxylic acid, carboxylic acid halide, ester, aldehyde, epoxide, amino alcohol, and acrylic, and R is a divalent organic radical.

5. A complex according to claim 1 that is not pyrophoric under ambient conditions.

6. An organoborane polyamine complex having the structure



wherein:

R^1 is an alkyl group having 1 to 10 carbon atoms;

R^2 and R^3 are independently selected from alkyl groups having 1 to 10 carbon atoms and phenyl-containing groups;

Am is a polyamine that comprises the reaction product of a diprimary amine-terminated material and a material having at least two groups reactive with primary amine, wherein a majority of the terminal groups in the polyamine are primary amine; and

the value of v is selected so as to provide an effective ratio of primary amine nitrogen atoms to boron atoms in the complex.

7. An organoborane polyamine complex according to claim 6 wherein R^1, R^2 and R^3 are independently selected from alkyl groups having 1 to 5 carbon atoms.

8. An organoborane polyamine complex according to claim 7 wherein R^1, R^2 and R^3 are the same.

9. An organoborane polyamine complex according to claim 6 wherein the polyamine is polyoxyalkylenediamine.

10. An organoborane polyamine complex according to claim 9 wherein the polyoxyalkylenediamine has the structure $H_2NR^4O-(R^5O)_w—(R^6O)_x—(R^5O)_y—R^4NH_2$ wherein

R^4, R^5, and R^6 are alkylene groups having 1 to 10 carbon atoms and which may be the same or which may be different;

w is ≥ 1;

x is ≥ 0; and

y is ≥ 0.

11. An organoborane polyamine complex according to claim 10 wherein R^4 is an alkyl group having 2 to 4 carbon atoms, R^5 is an alkyl group having 2 or 3 carbon atoms, and R^6 is an alkyl group having 2 or 3 carbon atoms.

12. An organoborane polyamine complex according to claim 6 wherein the polyamine is a linear

alkyldiamine in which the alkyl group has from 1 to 12 carbon atoms.

13. An organoborane polyamine complex according to claim 6 wherein the material having at least two groups reactive with primary amine has the structure Y-R-Z wherein Y and Z are moieties independently selected from the group consisting of carboxylic acid, carboxylic acid halide, ester, aldehyde, epoxide, amino alcohol, and acrylic, and R is a divalent organic radical.

14. An organoborane polyamine complex according to claim 13 wherein Y and Z are the same and the complex is substantially linear.

15. An organoborane polyamine complex according to claim 6 wherein the ratio of primary amine nitrogen atoms to boron atoms in the complex is about 0.5:1 to 4:1.

16. An organoborane polyamine complex according to claim 15 wherein the ratio of primary amine nitrogen atoms to boron atoms in the complex is about 1:1.

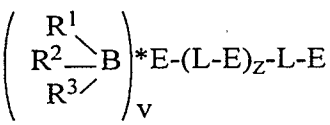
17. A system capable of initiating the polymerization of an acrylic monomer, the system comprising:

a) a complex comprising organoborane and polyamine, the polyamine comprising the reaction product of a diprimary amine-terminated material and a

material having at least two groups reactive with primary amine, wherein a majority of the terminal groups in the polyamine are primary amine; and

b) an effective amount of a compound that is reactive with amine for liberating the organoborane.

18. A system according to claim 16 wherein the complex has the structure



wherein:

R^1 is an alkyl group having 1 to 10 carbon atoms;

R^2 and R^3 are independently selected from alkyl groups having 1 to 10 carbon atoms and phenyl-containing groups;

$E-(L-E)_z-L-E$ is a polyamine wherein:

each E is the residue of a material that is selected from the group consisting of:

(a) polyoxyalkylenediamine having the structure $H_2NR^4O-(R^5O)_w—(R^6O)_x—(R^5O)_y—R^4NH_2$ wherein

R^4, R^5, and R^6 are alkylene groups having 1 to 10 carbon atoms and which may be the same or which may be different;

w is ≥ 1;

x is ≥ 0;

y is ≥ 0; and

(b) linear alkyldiamine in which the alkyl group has from 1 to 12 carbon atoms; and

each L is a linking group that is the residue of a material having the structure Y-R^7-X, wherein Y and X are independently selected from the group consisting of carboxylic acid, carboxylic acid halide, ester, aldehyde, epoxide, amino alcohol, and acrylic, and R^7 is a divalent organic radical

$z \geq 0$; and

the value of v is selected so as to provide an effective ratio of primary amine nitrogen atoms to boron atoms in the complex.

19. A system according to claim 18 wherein:

R^1, R^2 and R^3 are alkyl groups having 1 to 5 carbon atoms and are the same;

R^4 is an alkyl group having 2 to 4 carbon atoms;

R^5 is an alkyl group having 2 or 3 carbon atoms;

R^6 is an alkyl group having 2 or 3 carbon atoms;

Y and X are the same and are selected from the group consisting of epoxide, acrylic and carboxylic acid;

the value of v is selected such that the ratio of to primary amine nitrogen atoms to boron atoms in the complex is about 1:1 to 2:1; and

the complex is a liquid at room temperature and is substantially linear.

20. A system according to claim 18 wherein the compound that is reactive with amine for liberating

organoborane is selected from the group consisting of isocyanate, acid, acid chloride, sulfonyl chloride, and aldehyde.

21. A system according to claim 20 wherein the compound that is reactive with amine for liberating organoborane is acrylic acid or methacrylic acid.

22. A polymerizable acrylic composition comprising:

a) at least one acrylic monomer;

b) an effective amount of a complex comprising organoborane and and polyamine, wherein the polyamine comprises the reaction product of a diprimary amine-terminated material and a material having at least two groups reactive with primary amine, wherein a majority of the terminal groups in the polyamine are primary amine; and

c) an effective amount of a compound that is reactive with amine for liberating the organoborane to initiate polymerization of the at least one acrylic monomer.

23. A polymerizable acrylic composition according to claim 22 wherein the at least one acrylic monomer is selected from the group consisting of monofunctional acrylate ester, monofunctional methacrylate ester, substituted derivatives of the foregoing, and blends of the foregoing.

24. A polymerizable acrylic composition according to claim 23 wherein the monofunctional methacrylate ester is selected from the group consisting of methyl methacrylate, ethyl methacrylate, methoxy ethyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, cyclohexyl methacrylate, tetrahydrofurfuryl methacrylate, and blends thereof.

25. A polymerizable acrylic composition according to claim 22 wherein the at least one acrylic monomer comprises a blend of methyl methacrylate and butyl acrylate.

26. A polymerizable acrylic composition according to claim 22 further comprising an elastomeric modifier.

27. A polymerizable acrylic composition according to claim 22 wherein the composition comprises about 0.03 to 1.5 weight % boron.

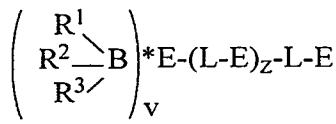
28. A polymerizable acrylic composition according to claim 27 wherein the composition comprises about 0.1 to 0.3 weight % boron.

29. A polymerizable acrylic composition according to claim 22 wherein the compound that is reactive with amine for liberating organoborane is selected from the group consisting of acid, isocyanate, acid chloride, sulfonyl chloride, and aldehyde.

30. A polymerizable acrylic composition comprising:

a) at least one acrylic monomer;

b) an effective amount of an organoborane polyamine complex having the structure



wherein:

R^1 is an alkyl group having 1 to 10 carbon atoms;

R^2 and R^3 are independently selected from alkyl groups having 1 to 10 carbon atoms and phenyl-containing groups;

each E is the residue of a diprimary amine-terminated material;

each L is the residue of a material having at least two groups reactive with primary amine;

$z \geq 0$; and

the value of v is selected so as to provide an effective ratio of primary amine atoms to boron atoms in the complex; and

c) an effective amount of compound that is reactive with amine for liberating the organoborane to initiate polymerization of the at least one organic monomer.

31. A polymerizable acrylic composition according to claim 30, wherein each E is the residue of polyoxyalkylenediamine.

32. A polymerizable acrylic composition according to claim 30, wherein each E is the residue of a linear alkyldiamine in which the alkyl group has from 1 to 12 carbon atoms.

33. A polymerizable acrylic composition according to claim 30, wherein each L is the residue of a material having the structure Y-R-X wherein Y and X are moieties independently selected from the group consisting of carboxylic acid, carboxylic acid halide, ester, aldehyde, epoxide, amino alcohol, and acrylic, and R is a divalent organic radical.

34. A polymerizable acrylic composition according to claim 30 wherein the compound reactive with amine for liberating organoborane is acrylic acid or methacrylic acid.

35. A composite article comprising a first substrate, and a second substrate bonded to the first substrate by an adhesive, wherein the adhesive comprises the the polymerized acrylic composition of claim 30.

36. A bonded composite according to claim ~~31~~ 35 wherein the first substrate is selected from the group consisting of polyethylene, polypropylene and polytetrafluoroethylene.

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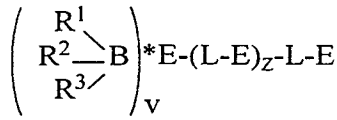
37. A polymerizable acrylic composition comprising:

a) a blend of acrylic monomers comprising alkyl acrylate monomer and alkyl methacrylate monomer;

b) a substantially linear organoborane polyamine complex having the structure



wherein:

R^1, R^2 and R^3 are alkyl groups having 1 to 5 carbon atoms and are the same;

E-$(L\text{-}E)_z$-L-E is a polyamine wherein:

each E is the residue of a material that is selected from the group consisting of:

(a) polyoxyalkylenediamine having the structure $H_2NR^4O\text{-}(R^5O)_w\text{—}(R^6O)_x\text{—}(R^5O)_y\text{—}R^4NH_2$ wherein

R^4, R^5, and R^6 are alkylene groups having 1 to 10 carbon atoms and which may be the same or which may be different;

w is ≥ 1;

x is ≥ 0;

y is ≥ 0; and

(b) linear alkyldiamine in which the alkyl group has from 1 to 12 carbon atoms; and

each L is a linking group that is the residue of a material having the structure Y-R^7-X, wherein Y and X are the same and are selected from the group consisting of carboxylic acid, carboxylic acid

halide, ester, aldehyde, epoxide, amino alcohol, and acrylic, and R^7 is a divalent organic radical;

$z \geq 0$; and

the value of v is selected such that the ratio of primary amine atoms to boron atoms in the complex is about 1:1 to 2:1; and

c) an effective amount of acrylic acid or methacrylic acid for liberating the organorborane in the complex to initiate polymerization of the blend of acrylic monomers.

38. A polymerizable acrylic composition according to claim 37 comprising about 0.03 to 1.5 weight % boron.

39. A polymerizable acrylic composition according to claim 38 comprising about 0.1 to 0.3 weight % boron.

40. A composite article comprising a first substrate, and a second substrate bonded to the first substrate by an adhesive, wherein the adhesive comprises the the polymerized acrylic composition of claim 37 and further wherein both the first and second substrates are independently selected from the group consisting of polyethylene, polypropylene and polytetrafluoroethylene.

41. A method of initiating the polymerization of an acrylic monomer, the method comprising the steps of:

a) providing at least one acrylic monomer;

b) blending the at least one acrylic monomer with a polymerization initiator system comprising :

i) a complex comprising organoborane and polyamine, wherein the polyamine comprises the reaction product of a diprimary amine-terminated material and a material having at least two groups reactive with primary amine, wherein a majority of the terminal groups in the polyamine are primary amine ;

ii) an effective amount of a compound that is reactive with amine for liberating the organoborane to initiate polymerization of the at least one acrylic monomer; and

c) initiating polymerization of the at least one acrylic monomer.

42. A method of bonding a polymer having a surface energy of less than 45 mJ/m^2 to a substrate, the method comprising the steps of :

a) providing a polymer having a surface energy of less than 45 mJ/m^2 ;

b) providing a substrate ;

c) providing an adhesive composition comprising :

i) at least one acrylic monomer ;

ii) an effective amount of a complex comprising organoborane and polyamine, wherein the polyamine comprises the reaction product of a diprimary amine-terminated material and a material having at least two groups reactive with primary amine, wherein a majority of the terminal groups in the polyamine are primary amine ; and

iii) an effective amount of a compound that is reactive with amine for liberating the organoborane to initiate polymerization of the at least one acrylic monomer;

d) applying the adhesive composition to either the polymer having a surface energy of less than 45 mJ/m^2 or the substrate ;

e) joining the polymer having a surface energy of less than 45 mJ/m^2 and the substrate with the adhesive composition therebetween ; and

f) permitting the adhesive composition to cure to adhesively bond the polymer having a surface energy of less than 45 mJ/m^2 and the substrate.