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DESCRIPTION

Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to adhesive compositions suitable for anchoring or fixing elements in a base or structural body as defined in the appended claims. More specifically, the present invention is directed towards adhesive compositions that are especially well suited for curing such compositions at lower temperatures, without compromising desirable characteristics such as strength and durability.

2. Discussion of the Related Art

[0002] It is well known that adhesive systems are useful for fixing or anchoring materials in or to rock, masonry, and concrete. Such systems typically involve the use of synthetic resins and monomers that are maintained separately from a hardening or curing agent until they are combined at or near the point of fastening. A variety of additional and often optional adjuvants may also be used with adhesive systems.

[0003] By way of example, U.S. Patent 5,157,072 to Hense, et al., teaches ethylenically unsaturated, substituted cycloaliphatic compounds as monomers and resins for minimizing shrinkage of the adhesive when used for anchoring bolts in bore holes. However, Hense, *et al.*, is silent on low shrinkage stress. U.S. Pat. No. 5,288,767 to Cramer, et al., teaches a methacrylate monomer in the first component together with diluent monomers. One of the stated goals of this patent is to eliminate styrene as a co-monomer, but Cramer, *et al.*, is silent on the subject of low-temperature curing. U.S. Pat. No. 6,037,408 to Weber, et al., is similar to the Cramer '767 patent, but it requires the use of very high levels of monomer and is silent on the affects of low temperature cure. Variously, U.S. Pat. No. 6,583,259, to Weber, et al., is concerned with adhesives to bond to wet bore holes; U.S. Pat. No. 7,544,739, to Liu, et al., teaches a composition for use under conditions of elevated temperatures; and U.S. Pat. No. 5,077,324, to Kistner, et al., is concerned with extending the shelf life the formulation prior to use. Neither any of the foregoing, nor a great many other references are directed towards adhesive compositions that are suitable for curing at low temperatures. AU Patent Publication No. 2010/200120 A1 describes a method for improving adhesion to moist boreholes in a

cementitious substrate by using methacryloxyalkyltrialkoxysilane chemicals. The use of alkoxysilanes is well known in the arts to improve adhesion in damp cementitious substrates, and is commonly used in adhesives and coatings. U.S. Pat. No. 6,583,259, to Weber, et al., mentions acetoacetoxyethyl methacrylate (AAEM) simply as a co-monomer, with no indication of its use other than as a diluent. U.S. Patent Publication No. 2006/045630 A1 describes the combination of acetoacetoxyalkyl (meth)acrylate and hydroxyalkyl (meth)acrylate as a combination that improves adhesion to a variety of different mineral substrates, but discloses that two-component mortar compositions that "... contain acetoacetoxyalkyl (meth)acrylates as reactive diluents, do not exhibit satisfactory adhesion values if they are used on concrete..." U.S. Patent Publication No. US 2007/299180 discloses the use of acetoacetoxyethyl methacrylate and organofunctional silanes in a waterborne latex emulsion polymer used for coatings, caulks, and sealants. Due to high shrinkage, waterborne latex emulsion polymers cannot provide adequate load for anchoring elements into a structural body. The disclosed use of acetoacetoxyethyl methacrylate is to provide crosslinking in the system, not adhesion under low temperature conditions. It is known that organofunctional silanes will hydrolyze during polymerization, and provide some crosslinking as the hydrolyzed silanes join, but may compromise adhesion to damp concrete, where the water in the latex paint dampens the concrete. All of the chemicals mentioned in the disclosure are reacted in enclosed vessels under very controlled conditions, none of which would be suitable for use in curing in a borehole to anchor an element to a structural body, let alone under low-temperature curing conditions. U.S. Pat. No. 6,037,408, to Weber, et al., describes reducing the shrinkage in a two-component adhesive fastening system by using a low shrinkage reactive monomer, 2,2-bis-[4-(methacryloxy-ethoxy)phenyl]propane as the primary ingredient. Other high molecular weight, low shrinkage monomers are identified to be used in conjunction with the foregoing monomer. Key to the disclosure is that the high percentage (51-99%) of reactive chemicals in the formulation must be high molecular weight and low shrinkage. There is no mention of possible use of acetoacetoxyethyl methacrylate or alkoxysilanes.

[0004] It is often the case that adhesives must be applied to anchoring elements in concrete and masonry under adverse weather conditions involving low temperatures and/or excess moisture. Unfortunately, it is not until the arrival of warmer weather at some later point in time that weakness or failure of the anchoring elements are observed. The effects of warming the substrate have been largely ignored in the past. Often, products that are developed for cold environments make the assumption that the substrate will not warm appreciably. Another tactic that has often been employed is to produce multiple variations of a product where several closely related compositions are developed, each associated with a specific temperature range. Under new protocols, however, the costs for testing can be prohibitive for a product line with multiple adhesives.

SUMMARY OF THE INVENTION

[0005] In light of the foregoing, it is desirable to provide an adhesive composition that not only can be cured at low temperatures, but that also exhibits good strength and structural integrity

over a wide range of temperature conditions. Moreover, another disadvantage of many adhesive compositions that are currently commercially available is that they contain or include phthalates. Phthalates, or phthalate esters, are often used in adhesive formulations as phlegmatizing agents to prevent the rapid and explosive reaction of certain curing agents when they are physically disturbed. Over concerns related to health reasons, however, phthalates are being phased out of many products in the United States, Canada, Europe and elsewhere in the world. Accordingly, it is desirable to provide an adhesive composition that does not include phthalates yet does not compromise safety.

[0006] The present invention provides an adhesive composition for anchoring elements as defined in the appended claims 1 to 11.

DETAILED DESCRIPTION OF THE INVENTION

[0007] The present invention provides an adhesive composition for anchoring materials in or to concrete or masonry. The materials to be anchored in or to concrete or masonry include, but are not limited to: metallic objects such as steel rods and steel bolts; ceramics; other concrete or masonry members; plastics; glasses; and woods.

[0008] As indicated above, one of the motivating factors for the present invention was to develop an adhesive composition that cured at low temperatures without compromising strength of the adhesive. In the course of developing such a composition, it was also recognized that it might also be possible to impart other desirable features to the adhesive composition. Thus, it was postulated that the inclusion of a silane group, for example, might help promote adhesion of the composition to a cementitious substrate in wet or humid conditions. In addition, it was felt that an acetoacetoxy functional group might help promote adhesion of the composition to the insert, the substrate, or both. Under most conditions, these two monomers do not appear to significantly improve performance of an anchoring adhesive. Surprisingly, however, it was found that the presence of both an acetoacetoxy moiety and a silane moiety can provide a synergistic effect when curing takes place at low temperatures. Use of these monomers has unexpectedly resulted in demonstrably better curing at low temperatures. For instance, when acetoacetoxyethyl methacrylate and methacryloxypropyl trimethoxysilane (MPTMS) are used together in a first adhesive composition, a 20% improvement in mechanical strength has been observed when the adhesive was cured at low temperatures and then warmed to standard temperature.

[0009] Quite surprisingly, during the development of the inventive adhesive compositions described herein, it has also been discovered that the synergistic effect obtained upon the combination of silane and acetoacetoxy moieties is unexpectedly enhanced by the presence of a phthalate-free free radical initiator. Remarkably, the inventive adhesive compositions described herein have been shown to be curable at low temperatures, without any compromise as to strength, durability or structural integrity whether at low, moderate or elevated temperatures. In other words, the inventive silane-containing, and acetoacetoxy-containing

compositions described herein, which can additionally be prepared phthalate-free, may be cured at low temperatures and yet retain the ability to perform at least as well as--if not better than--commercially available adhesive compositions, whether at low, moderate or elevated temperatures. The use of phthalate-free components in the inventive formulations can result in an approximately 10% increase in strength and durability characteristics following cure at low temperatures.

Reactive Resin

[0010] In discussing resins and monomers herein, it is to be understood that these terms may be used interchangeably. The molecules which are often referred to as resins are in reality high molecular weight monomers, from a chemistry standpoint. However, the terms resin and monomer are often used interchangeably in the adhesives trade and thus the terms are used without chemical distinction herein. No limitation(s) are intended or implied in the inventive adhesive compositions based on such terminology.

[0011] The inventive adhesive compositions comprise at least one synthetic resin or polymerizable monomer selected from among: allylic resins; bismaleimide resins; epoxy acrylate resins; epoxy methacrylate resins; phenolic-based acrylates; phenolic-based methacrylates; unsaturated polyester resins; urethane acrylate resins; urethane methacrylate resins; and vinyl ester resins. In one embodiment, one of the synthetic resins is preferably an alkoxyated bisphenol or a novolac compound having one or more functional acrylate or methacrylate groups. A novolac-also spelled novolak-is a phenol-aldehyde condensation prepolymer obtained by condensing phenolic monomers with a stoichiometric deficiency of aldehydes.

[0012] In one aspect, an adhesive composition of the present invention includes at least one polymerizable monomer that contains or includes at least one functional group selected from among: acrylates; methacrylates; as well as combinations thereof; in combination with a phenolic selected from among; bisphenol A; bisphenol F; bisphenol S; novolac monomers; and combinations thereof. In a preferred aspect of the invention, the reactive resin includes an alkoxy group. In a more preferred aspect of the invention, the alkoxy group(s) is positioned in the reactive resin between the phenolic and the acrylate or methacrylate group(s). Especially preferred for use with the present invention are alkoxyated methacrylates and alkoxyated dimethacrylates, with ethoxyated bisphenol A dimethacrylate being particularly preferred.

[0013] Ethoxyated bisphenol A dimethacrylate resins with no more than 4 mole ethoxylation are particularly suitable for use in the first composition of the inventive adhesive formulations of the present invention. Degrees of condensation of ethylene oxide groups from about 1.0 mole to about 4.0 mole are preferred, with an average degree of condensation of about 2.0 mole to above 4.0 mole being more preferred. This resin is difunctional and has relatively few ethoxylate groups, thus it has good crosslink density, which results in high mechanical strength. This monomer also has a high glass transition temperature, T_g , which allows for higher end

use temperatures of the adhesive. It also has a very high molecular weight and subsequently exhibits very low shrinkage stress. Without being bound by theory, the ethoxylate groups are believed to help promote adhesion to cementitious substrates.

Diluent Monomer

[0014] Diluent monomers, also called reactive diluents, are often used in adhesive compositions to bring the viscosity of a reaction mixture into a desirable range. Such diluents are also used to incorporate functionality to improve the adhesion of these compositions to the insert, the substrate, or both. Both multifunctional and monofunctional diluents may be used with the low temperature curable compositions of the present invention. Multifunctional diluents can be used to impart greater crosslink density which can improve chemical resistance, moisture tolerance and performance at higher use temperatures. Accordingly, either liquid or solid reactive organic diluents may be used with the reactive resins described herein to provide viscosity control, impart functionality, and/or increase the cross-linking density of the reaction mixture; as such, use of diluent monomers is only required for reaction mixtures in which the afore mentioned properties must be altered. If a diluent monomer is used it is therefore desirable that the diluent monomer contain at least one functional group that is reactive with the polymerizable monomer described above. High molecular weight is also desirable in a diluent monomer; high molecular weight minimizes shrinkage stress and imparts low volatility. Reactive diluents are optional for the present invention; however, those reactive diluents suitable for use with the adhesive compositions of the present invention include ethylenically unsaturated monomers. Among ethylenically unsaturated monomer diluents that can be used with the present invention, it is preferred that the reactive organic diluent include at least one monofunctional monomer to lower viscosity and at least one multi-functional monomer to increase crosslink density. As with the reactive resin, polar groups such as alkoxylates; carbonyls; ether linkages; ester linkages; hydroxyls; amines; and amides are believed to improve adhesion to the substrate.

[0015] As indicated above, monofunctional monomers may also be used with the inventive adhesive formulations. Suitable monofunctional monomers for use with the present invention include, but are not limited to: methyl methacrylate, isopropyl methacrylate, isobutyl methacrylate, tert-butyl methacrylate, steryl methacrylate, 2-phenoxyethyl methacrylate, tetrahydrofurfuryl methacrylate, glycidyl methacrylate, isobornyl methacrylate, hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxybutyl methacrylate, benzyl methacrylate, dicyclopentyl methacrylate, tert-butyl acrylate, steryl acrylate, 2-phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, isobornyl acrylate, hydroxybutyl methacrylate, benzyl acrylate, dicyclopentyl acrylate, and the like, as well as combinations thereof.

[0016] Multifunctional monomers that are suitable for use with the present invention include, but are not limited to: ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, 1,3-butylene glycol

dimethacrylate, 1,4-butanediol dimethacrylate, 1,6-hexanediol dimethacrylate, neopentyl glycol dimethacrylate, cyclohexane dimethanol dimethacrylate, dicyclopentyl dimethacrylate, glyceryl trimethacrylate, trimethylolpropane trimethacrylate, pentaerythritol trimethacrylate, pentaerythritol tetramethacrylate, dipentaerythritol pentamethacrylate, ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, dipropylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,6-hexanediol diacrylate, neopentyl glycol diacrylate, cyclohexane dimethanol diacrylate, dicyclopentyl diacrylate, glyceryl triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, pentaerythritol tetraacrylate, dipentaerythritol pentaacrylate, tris(2-hydroxy ethyl)isocyanurate triacrylate, alkoxylated variations of the foregoing monomers, and the like, as well as any combinations thereof. Additionally metallic acrylates and methacrylates can be used to increase crosslink density these include, but are not limited to acrylates and methacrylates of zinc, magnesium and calcium.

[0017] Other monomers, such as vinyl, allylic and acrylamide monomers may also be used. Examples of these monomers which can be used with the present invention include, but are not limited to: styrene; vinyl toluene; methyl styrene; divinyl benzene; allyl methacrylate; allyl cinnamate; allyl glycidyl ether; acrylamide; methacrylamide; N-methylol acrylamide; N-methylol methacrylamide; as well as combinations thereof. The use of vinyl, allylic, and acrylamide monomers with the inventive compositions described herein is not preferred, however, due to possible health concerns.

[0018] Preferred diluent monomers for the present invention include: hydroxypropyl methacrylate, isobornyl methacrylate, tert-butyl methacrylate, methyl methacrylate, tetrahydrofurfuryl methacrylate, benzyl methacrylate, ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, tris(2-hydroxyethyl) isocyanurate triacrylate, and trimethylolpropane triacrylate. Tetrahydrofurfuryl methacrylate and trimethylolpropane trimethacrylate are particularly preferred.

Acetoacetoxy Functional Monomer

[0019] As indicated above, the use of an acetoacetoxy functional monomer has surprisingly been found to provide an unexpected, beneficial synergistic effect with respect to curing at low temperature when used in the presence of a monomer that contains a cross-linkable silane group. In addition to the main monomer described above, the adhesive compositions of the present invention therefore also comprise an ethylenically unsaturated monomer that contains at least one cross-linkable acetoacetoxy functional group. Acetoacetoxy functionality can be incorporated into the polymer matrix in the inventive adhesives using acetoacetoxy alkyl acrylates such as, but not limited to: acetoacetoxyethyl acrylate; acetoacetoxyethyl methacrylate; diacetone acrylamide; acetoacetoxy vinyl ether; as well as combinations of any of the foregoing. A preferred reactive monomer diluent is acetoacetoxyethyl methacrylate, often abbreviated AAEM.

Silane Monomer

[0020] As indicated above, the adhesive compositions of the present invention also comprise an ethylenically unsaturated monomer that contains at least one cross-linkable silane group. Cross-linkable silane groups that are preferred for use with the inventive compositions comprise hydrolizable alkoxy groups. Examples of hydrolizable alkoxy groups that are suitable for use with the present invention may be selected from among: hydroxy group; halogen atom; alkoxy group; and acyloxy group; as well as combinations of any of the foregoing. Silane monomers having alkoxy groups are preferred.

[0021] Examples of monomers having both a point of polymerizable unsaturation and a cross-linkable silicon group include: methacryloxypropyl polyalkoxy silanes such as methacryloxypropyl trimethoxysilane, methacryloxypropylmethyl dimethoxy silane and methacryloxypropyl triethoxy silane; acryloxypropyl polyalkoxy silanes such as acryloxypropyl trimethoxy silane, acryloxypropylmethyl dimethoxy silane, and acryloxypropyl triethoxy silane; vinylalkyl polyalkoxy silanes such as vinyl trimethoxysilane, vinylmethyl dimethoxy silane and vinyl triethoxy silane; as well as combinations of any of the foregoing.

Curing Agent

[0022] Curing agents in the present invention are free-radical initiators used with adhesive compositions in order to initiate polymerization and provide cross-linking of the adhesive. In the appended claims, peroxides that are suitable for use with the present invention include dibenzoyl peroxides

[0023] Non-reactive diluents are often used with dibenzoyl peroxide to add stability to the product. Examples of non-reactive diluents used to stabilize dibenzoyl peroxide include, but are not limited to: di-n-butyl phthalate; diisobutyl phthalate; dicyclohexyl phthalate; butylbenzylphthalate; trialkylphosphates; triarylphosphates; alkylarylphosphates; alkyl ethers of mono and diethylene glycols, alkyl ethers of mono and dipropylene glycols; benzoates of mono and diethylene glycols; benzoates of mono and dipropylene glycols; water; and the like. Additionally, non-reactive diluents such as ethylene glycol, propylene glycol, glycerol, urea and the like are often used to lower the freezing point of benzoyl peroxide mixtures. In one aspect of the present invention phthalate-free dibenzoyl peroxide mixtures are preferred.

Accelerants

[0024] Accelerants are also used with the adhesive compositions of the present invention.

[0025] Accelerators suitable for use herein may be selected from among: N,N-diisopropanol-p-

toluidine, N,N-dihydroxyethyl-p-toluidine; N,N-methylhydroxyethyl-p-toluidine; and mixtures of the foregoing.

Fillers

[0026] Adhesive compositions that are used for anchoring members often contain fillers to both impart strength and reduce cost. As will be appreciated by those knowledgeable in the relevant art, fillers can also be used to control viscosity. Fillers that are appropriate include, but are not limited to: silica fume; quartz sand; finely ground quartz; a metal oxide such as magnesium oxide, iron oxide, aluminum oxide, and calcium oxide; clinker; calcium carbonate; metal shavings or particles; barium sulfate; aluminum trihydrate; wollastonite; kaolin clay; mica; feldspar; nepheline syenite; glass beads; corundum; talc; chalk; ceramic microspheres; and cement; in addition to combinations of any of the foregoing. In one example, either the first composition or the second composition comprising the inventive adhesives contains at least one filler, which may comprise the same or different fillers. In another example, both the first composition and the second composition contain fillers. In yet another example, the first component preferably contains at least one filler that is reactive with water, examples of which include cement and metal oxides. Cement is often a preferred filler, as it ties up water in the adhesive system and allows for better performance when an anchor is exposed to elevated temperatures after cure. As will be understood by those skilled in the relevant art, fillers may be mixed into the first, monomer component and/or the second, curing agent component of the inventive adhesives.

Inhibitors

[0027] Inhibitors are required to prevent polymerization of the monomers and resins of the first component during storage. Inhibitors are present in reactive resins and monomers as they are received from manufacturers; however, additional inhibitor is often required to improve shelf life of the final product or to counteract the presence of the accelerator. Polymerization inhibitors appropriate include, but are not limited to: methyl hydroquinone, hydroquinone, catechol, hydroquinone monomethyl ether, mono-tert-butyl hydroquinone, di-tert-butyl hydroquinone, p-benzoquinone, 2,5-diphenyl-p-benzoquinone, p-benzoquinone, trimethyl hydroquinone, naphthaquinone, di-tert-butyl methylphenol, and combinations of any of the foregoing.

Thixotropic Agents

[0028] Thixotropic agents are often used in adhesive compositions to reduce the tendency of the liquid resin to flow or drain from vertical surfaces. Thixotropic agents that are suitable for use with adhesive compositions include, but are not limited to: fumed silica, organosilicas, clays

and silicic acid. Commercially available fumed silicas that are particularly suitable for use are sold under such trademarks as Aerosil[®] available from Evonik Industries, and Cab-o-Sil[®] available from Cabot Corp.

Adjuncts

[0029] It is recognized that other components or adjuvants known to those skilled in the art may also optionally be included in the inventive adhesive compositions. Such components may include, but are not limited to: antifoaming agents; catalysts; coupling agents; non-reactive diluents; dyes; fillers; fungicides; impact modifiers; odor maskants; pigments; solvents; stabilizers; surfactants; wetting agents; as well as combinations of any of the foregoing.

Formulations

[0030] A number of different formulations that included varying amounts of the above active and optional ingredients were prepared and evaluated for curing at low and medium temperatures, and testing at low, medium and high temperatures. The term "low temperature" as used herein is understood to indicate temperatures on the order of approximately $-10\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ ($14\text{ }^{\circ}\text{F} \pm 4\text{ }^{\circ}\text{F}$). The term "medium temperature," "ambient temperature", "standard temperature" or "average temperature" as used herein is understood to refer to room temperature or temperatures of approximately $23\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ ($72\text{ }^{\circ}\text{F} \pm 4\text{ }^{\circ}\text{F}$). The term "high" or "elevated temperatures" as used herein is understood to indicate temperatures on the order of approximately $82\text{ }^{\circ}\text{C} \pm 3\text{ }^{\circ}\text{C}$ ($180\text{ }^{\circ}\text{F} \pm 4\text{ }^{\circ}\text{F}$). Thus, a variety of different reactive main monomers were used in combinations with acetoacetoxy-containing monomers, both with and without monomers that contained silane groups.

Phthalate-Free Compositions

[0031] As indicated above, formulations that comprised a reactive resin to which an acetoacetoxy-silane monomer combination was added were found to exhibit remarkably good strength and durability characteristics at room medium temperatures following curing at low temperatures. In many instances, the performance of these inventive adhesive compositions showed nearly a two-fold improvement over other formulations that did not include the acetoacetoxy-silane monomer combination. Even more unexpectedly, however, a further improvement in performance characteristics was observed when adhesive compositions were formulated without the presence of any phthalate moieties. Phthalate-free adhesive compositions of the present invention have surprisingly been found to be especially well-suited for curing at low temperatures. On average, the removal of phthalates from the inventive reactive resin/acetoacetoxy/silane monomer combination resulted in a 10% improvement in performance over adhesive compositions in which phthalates were included.

[0032] Phthalates are typically introduced into adhesive compositions with the free radical initiators that are used. According to one aspect of the present invention, therefore, noticeable improvements in adhesive performance can be observed in formulations at standard temperatures following cure at low temperatures when free radical initiators are used in the inventive adhesives that are phthalate-free. Examples of phthalate-free free-radical initiators that are suitable for use with the present invention include dibenzoyl peroxides. Phthalate-free dibenzoyl peroxides are commercially available under a variety of brand names such as, but not limited to, the Perkadox[®] series of free radical initiators available from Akzo Nobel and Luperox[®] series of free radical initiators from Elf Atochem.

EXAMPLES

[0033] A number of adhesive compositions were prepared in accordance with the teaching of the present invention for use in comparison to commercially available adhesive compositions. Performance characteristics were evaluated after cure at standard room temperature of 23 ± 4 °C (73 ± 8 °F) and at lower temperatures of -10 °C (14 °F) to mimic curing in cold conditions. Test members were prepared as follows. A channel or bore hole was created in a formed or smooth steel-troweled face of a Portland cement-based concrete test member of compressive strength in the range of 25.3 to 28.0 MPa (3,666 to 4,059 psi). The bore hole was made using a rotary-hammer drill with a 17.5 mm (11/16 inch) diameter carbide bit meeting the requirements of American National Standards Institute Bulletin 212.15 (ANSI B212.15, available in the United States from the Cemented Carbide Producers' Association). The bore hole was drilled to a depth of 79.4 mm (3.125 inch) embedment, perpendicular to the test surface. The channel chamber was then cleaned by blowing compressed air at 0.59 MPa (85 psi) into the hole for four seconds, followed by brushing the bore hole for four complete strokes using a nylon brush of greater diameter than the bore hole, followed by blowing compressed air at 0.59 MPa (85 psi) into the hole a second time, also for four seconds. The anchoring adhesive to be tested was then injected into the bore hole in such a manner as to ensure that the bore hole was evenly filled from the bottom of the chamber to a point approximately two-thirds full. A 15.9 mm (5/8 inch) diameter threaded metal rod was then inserted into the adhesive with a slight twisting motion and the adhesive and insert were allowed to cure undisturbed for one hour. After one hour, a load was placed on the metal rod anchors in tension until the point of failure in accordance with test methods in ASTM E488 as modified by ICC-ES Acceptance Criteria AC308. Tensile testing was performed using an in-house confined or restrained tension testing rig using a 13.6 kg (30 ton) hydraulic ram and a 22.7 kg (50 ton) load cell, in compliance with ASTM E488 as modified by ICC-ES Acceptance Criteria AC308. The confined test setup was used to maximize strain on the adhesive while minimizing the risk of concrete failure.

[0034] For the evaluation of inventive formulations after cure at lower temperature, another series of smooth-faced, steel-troweled Portland cement-based concrete test members were

prepared in a manner identical to the procedure outlined immediately above. The prepared test members were then placed into a controlled temperature chamber maintained at -10°C (14°F) and allowed to come to temperature equilibrium over the course of several days. The anchoring adhesive was then injected into the bore hole in the temperature controlled chamber, filling the drilled cavity from the bottom of the bore hole to a point approximately two-thirds full. A 15.9 mm (0.625 inch) diameter threaded metal rod was then inserted into the adhesive with a slight twisting motion and the adhesive and insert were left undisturbed and permitted to cure at -10°C (14°F) for twenty-four hours. At the end of that period, the test member was removed from the controlled temperature chamber and allowed to come to room temperature of approximately $23 \pm 4^{\circ}\text{C}$ ($73 \pm 8^{\circ}\text{F}$). The anchors were again loaded in tension until the point of failure in accordance with test methods in ASTM E488 as modified by ICC-ES Acceptance Criteria AC308, as indicated above. Tensile testing was performed using a confined or restrained tension test. The confined test setup was used to maximize strain on the adhesive while minimizing the risk of concrete failure.

[0035] Tables 1, 2 and 3 below contain the results of tensile tests performed on a variety of adhesive compositions that were cured at different temperatures in the manner described above. The compositions that were evaluated include commercially-available adhesive products as indicated in Table 1. Tables 2 and 3 contain a summary of a number of different formulations that were evaluated during the development of the inventive low-temperature cure compositions described herein.

[0036] Specifically and with reference to Table 1, the commercially available adhesives that were evaluated include: 1) HY 150 Max, manufactured by Hilti Aktiengesellschaft of Schaan, Liechtenstein, available in the United States online and through various distributors; 2) AC 100+ Gold™, available from Powers Fasteners, Inc., of Brewster, NY; 3) FIS VW from Fischerwerke GmbH and Co. KG of Waldachtal, Deutschland, not available in the United States; and 4) Sikadur® AnchorFix-1, from Sika AG of Baar, Switzerland, and available through various distributors in the United States. Both HY 150 Max and AC100+ Gold™ have approvals in the United States for installations under low temperature cure conditions. HY 150 Max, FIS VW and AnchorFix-1 have approvals in Europe for installations under low temperature cure conditions.

Table 1 Test Results for Competitive Products

Bond Strength After Cure (MPa)				
Company	Hilti	Powers	Fischer	Sika
Product	HY150 Max	AC100+ Gold	FIS VW	Anchorfix-1
Cure at 23°C , Test at 82°C	16.69	9.09	14.77	12.12
Cure at 23°C , Test at 23°C	21.95	16.32	18.62	15.44
Cure at -10°C , Test at 23°C	14.52	9.40	10.69	9.58

Bond Strength After Cure (MPa)				
Cure at -10°C, Test at -10°C	19.71	NE ^a	NE ^a	12.17
Low Temperature vs. Standard Temperature Degree of Cure ^b				
	66.2%	57.6%	57.4%	60.3%
Phthalates present?	Yes	Yes	Yes	Yes
Notes to Table 1 ^a NE - Not Evaluated ^b This calculated value is the ratio of the strength at 23 °C after cure at -10 °C compared to the strength at 23 °C after cure at 23 °C, expressed in percent.				

[0037] Table 2 contains a summary of representative formulations that were tested over a range of different concentrations combinations. The Examples in Table 2 are comparable in strength to the competitive products shown in Table 1.

Table 2 Formulations and Test Results of Example Compositions

Example	1	2	3	4	5	6
First Component						
Reactive Resin	22.4%	17.5%	22.3%	17.1%	17.1%	17.0%
Diluent monomer	15.2%	25.0%	15.1%	20.8%	20.8%	20.2%
Filler	60.2%	54.3%	59.8%	59.3%	59.2%	59.7%
Inhibitor	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%
Accelerator	0.2%	0.3%	0.8%	0.3%	0.4%	0.6%
Miscellaneous ^a	2.0%	2.9%	2.0%	2.5%	2.5%	2.5%
Second Component						
Free radical initiator	11.9%	13.0%	14.8%	14.6%	21.3%	14.5%
Nonreactive diluent	36.9%	40.2%	33.0%	35.6%	35.7%	35.6%
Filler	48.0%	43.5%	48.9%	45.6%	45.9%	45.3%
Miscellaneous ^a	3.2%	3.3%	3.3%	4.2%	5.1%	4.6%
Bond Strength After Cure (MPa)						
Cure at 23°C, Test at 82°C	13.04	10.31	10.99	11.05	9.57	12.88
Cure at 23°C, Test at 23°C	15.78	10.46	16.31	15.03	15.32	21.83
Cure at -10°C, Test at 23°C	7.99	4.96	11.52	10.26	9.21	13.50

Low Temperature vs. Standard Temperature Degree of Cure ^b						
	50.6%	47.4%	70.7%	68.3%	60.1%	61.9%
Phthalates present?	Yes	Yes	Yes	Yes	Yes	Yes

Notes to Table 2

^aSelected from among: pigments; thixotropes; dyes and colorants; etc.

^bThis value, calculated for the entries in the table from their bond strengths, is the ratio of the strength at 23 °C after cure at -10 °C compared to the strength at 23 °C after cure at 23 °C, expressed in percent.

[0038] Following the initial discovery that acetoacetoxy-silane monomers imparted discernable low-temperature cure improvements to the main reactive resins, a series of experiments were conducted using phthalate-free initiators. As these latter adhesive formulations exhibited even more remarkable strength characteristics at medium temperatures following low temperature cure, a number of experiments were conducted in order to evaluate alternate adhesive compositions. The results of these studies are summarized in Table 3 below. Examples A through C of Table 3 represent a preferred aspect of the present invention, in that they provide phthalate-free compositions well-suited for low temperature cure. In examples A and B the phthalate-free radical initiator used was Perkadox[®] L-40 RPS; and in example C the free radical initiator used was Perkadox[®] BTW50. Examples D through G represent an alternate aspect of the present invention in which the adhesive composition is not phthalate-free. Perkadox[®] 40e was used as the free radical initiator in examples D through G.

Table 3 Formulations and Test Results for Sample Compositions

Example	A	B	C	D	E	F	G
First Component							
Reactive Resin	18.0%	18.0%	18.0%	18.0%	16.8%	16.8%	13.6%
Acetoacetoxy monomer	1.7%	1.7%	1.7%	1.7%	3.2%	0%	0%
Silane monomer	0.5%	0.5%	0.5%	0.5%	0.9%	0.9%	1.0%
Diluent monomer	19.4%	19.4%	19.4%	19.4%	16.8%	20.0%	23.3%
Filler	57.3%	57.3%	57.3%	57.3%	59.2%	59.2%	59.3%
Inhibitor	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%	<0.1%
Accelerator	0.9%	0.9%	0.9%	0.9%	0.6%	0.6%	0.5%
Miscellaneous ^a	2.4%	2.4%	2.4%	2.4%	2.5%	2.5%	2.3%
Second Component							
Free radical initiator	14.5%	13.3%	14.6%	14.5%	14.5%	14.5%	14.6%
Nonreactive diluent	38.5%	39.0%	36.9%	35.6%	35.6%	35.6%	35.9%
Filler	41.9%	42.9%	43.7%	45.3%	45.3%	45.3%	45.5%

Second Component							
Miscellaneous ^a	5.1%	4.8%	4.8%	4.6%	4.6%	4.6%	4.0%
Bond Strength After Cure (MPa)							
Cure at 23°C, Test at 82°C	15.36	15.14	13.45	14.56	12.84	12.38	10.65
Cure at 23°C, Test at 23°C	22.28	20.77	18.98	21.49	21.55	21.07	20.35
Cure at -10°C, Test at 23°C	21.28	20.42	18.97	19.80	19.49	18.30	16.32
Cure at -10°C, Test at -10°C	22.10	21.73	NE ^b	21.65	NE ^b	NE ^b	NE ^b
Low Temperature vs. Standard Temperature Degree of Cure ^c							
	95.5%	98.3%	99.9%	92.1%	90.5%	86.9%	80.2%
Phthalates present?	No	No	No	Yes	Yes	Yes	Yes
Notes to Table 3 ^a Selected from among: pigments; thixotropes; dyes and colorants; etc. ^b NE - Not Evaluated ^c This value, calculated for the entries in the table from their bond strengths, is the ratio of the strength at 23 °C after cure at -10 °C compared to the strength at 23 °C after cure at 23 °C, expressed in percent.							

[0039] A number of different formulations were tried and evaluated for strength and performance characteristics after curing at different temperatures. In one series of experiments, adhesive formulations with different ratios/levels of AAEM and silane were prepared and evaluated. The different combinations that were tested include (expressed in terms of weight % composition): a) 1.67% AAEM with 0.5% silane; b) 1.67% AAEM with 1.5% silane; c) 5% AAEM with 1.67% silane and d) 5 % AEM with 1.5% silane). All of the foregoing formulations gave equivalent bond strengths when cured at -10°C and tested at 23°C.

Delivery Method

[0040] Many methods of delivery for adhesive compositions may be contemplated. For instance, adhesive components may be stored in relatively small amounts in multi-chambered cartridges from which components are dispensed simultaneously. Mixing may take place manually or through a static mixing nozzle. Alternately, the components may be stored separately in large containers and mixed with mechanical dispensers just prior to use. Often, the selection of reactive resin and any diluent monomers may need to reflect the delivery method or tool that will be used to introduce the adhesive into a substrate. Dispensing with manual tools presents challenges, especially for low temperature cure adhesives. It is

therefore desirable that the viscosities of such adhesive formulations can be adjusted in order to enable the end user to easily install the adhesive under low temperature conditions. In general, low viscosity reactive resins are preferred for such applications. However, low viscosity can also be achieved through a combination of choice of reactive resin, choice and amount of diluent monomer, and amount of filler. Accordingly, and as will be understood by those skilled in the relevant art, the ingredients of the present invention may be formulated over a wide range in order to meet a variety of viscosity criteria from water-thin to thick paste.

[0041] In an example, a delivery method for the inventive adhesive compositions comprises using a dual chamber cartridge to dispense the composition through a static mixing nozzle using a dispensing tool. The dispensing tool can be of any power configuration including, but not limited to manual, electric, battery operated or pneumatic. In one example, the first and second components are each prepared separately and then combined by mixing their ingredients in a large mechanical mixer. In one example, the components are placed in separated multi-component, side-by-side or coaxial adhesive cartridges for use in the field where they are dispensed through a static mixing nozzle using a dispensing tool.

[0042] An alternate delivery method for an adhesive composition prepared according to the present invention may involve delivering the two separate components in the field using dual tank bulk dispensing equipment. Yet another delivery method for an adhesive composition according to the present invention would involve the use of frangible capsules. Thus a first, sealed capsule containing a first component of the inventive formulations may be situated inside a second, larger capsule. The second capsule also contains the second component of the formulation and is also sealed. In the field, such a dual capsule would be placed into a bore hole and broken by either driving an anchor element through the dual capsule or spinning the anchor element into the dual capsule. In such a frangible capsule delivery system, the dual capsules become part of the adhesive and serve as a filler. Regardless of the delivery technique employed, according to one aspect of the present invention, the first and second components are mixed in amounts such that the weight ratio of the first component to the second component is approximately ten to one. In another example, the first component makes up approximately 91% of the total composition and the second component makes up approximately 9% of the total composition.

[0043] In one aspect, the formulations of the present invention improve upon adhesives of the prior art by providing an adhesive formulation that has high internal mechanical strength, high bond strength with the base and the anchor, absorbs little water, has low toxicity, a viscosity appropriate for filling bore holes, and at the same is suitable for curing at low temperatures. In another aspect, the formulations of the present invention, when applied and cured at low temperature, exhibit strength and durability characteristics at both room temperatures and elevated temperatures that are at least equivalent to adhesives that are currently commercially available. That is, equivalent strength and durability characteristics of the instant formulations can be realized both at room temperatures and elevated temperatures as compared to commercially available adhesives, without the need for formulating compositions differently for use at different temperatures. Moreover, the inventive adhesive compositions provide the

added advantage that they are phthalate free.

REFERENCES CITED IN THE DESCRIPTION

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Patentkrav

1. En hærdelig klæbemiddelssammensætning til fastgøring af elementer i et strukturelt legeme, omfatter:

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- a. mindst en reaktiv resin, hvori den reaktive resin er udvalgt iblandt: allyliske resiner; bismaleimid resiner; epoxyacrylat resiner; epoxymethacrylat resiner; phenolbaserede acrylater; phenolbaserede methacrylater; umættede polyester resiner; urethanacrylat resiner;

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- urethanmethacrylat resiner; og vinylester resiner; såvel som kombinationer af enhver ovenstående;

- b. mindst en funktionel acetoacetoxymonomer;

- c. mindst en silanmonomer;

- d. en fri radikal initiator; og

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- e. en accelerator;

i hvilken den frie radikal initiator er dibenzoylperoxid, og acceleratoren er udvalgt fra gruppen bestående af: N,N-diisopropanol-p-toluidin; N,N-dihydroxyethyl-p-toluidin; N,N-methylhydroxyethyl-p-toluidin; og kombinationer deraf.

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2. Sammensætningen ifølge krav 1, hvori vedhæftningsstyrken af klæbemidlet ved 23 °C efter hærkning ved -10 °C sammenlignet styrken af klæbemidlet ved 23 °C efter hærkning ved 23 °C er større end 50%, fortrinsvist større end 60%, mere fortrinsvist større end 70% og mest fortrinsvist større end 80%; hvori bindingsstyrken er vurderet ved træktest af indesluttet forankring i overens-

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stemmelse med ASTM E488.

3. Sammensætningen ifølge krav 1, hvori efter hærkning ved -10 °C, klæbemidlet udviser en bindingsstyrke ved 23 °C som er større end 10 MPa, fortrinsvist større end 12 MPa, mere fortrinsvist større end 14 MPa og mest fortrinsvist større end 16 MPa; hvori bindingsstyrken er vurderet ved træktest af indesluttet forankring i overensstemmelse med ASTM E488.

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4. Sammensætningen ifølge krav 1, hvori:

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- b. den funktionelle acetoacetoxymonomer er udvalgt iblandt: acetoacetoxyethyl acrylat; acetoacetoxyethylmethacrylat,

diacetoneacrylamid; acetoacetoxy vinyl ether; såvel som kombinationer af enhver af ovenstående; og

c. silanmonomeren er udvalgt iblandt:

methacryloxypropyltrimethoxysilan; methacryloxypropylmethyldimethoxysilan; methacryloxypropyltriethoxysilan; acryloxypropyltrimethoxysilan; acryloxypropylmethyldimethoxysilan; acryloxypropyltriethoxysilan; vinyltrimethoxysilan; vinylmethyldimethoxysilan; vinyltriethoxysilan; såvel som kombinationer af enhver af ovenstående.

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5. Sammensætningen ifølge krav 1, yderligere omfatter:

f. mindst en reaktiv fortyndende monomer, hvori den fortyndende monomer er udvalgt iblandt: monofunktionelle monomerer, multifunktionelle monomerer, og kombinationer af ovenstående; hvori:

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1) Den monofunktionelle monomer er udvalgt iblandt:

methylmethacrylat; isopropylmethacrylat; isobutylmethacrylat; tert-butylmethacrylat; sterylmethacrylat; 2-phenoxyethylmethacrylat; tetrahydrofurfurylmethacrylat; glycidylmethacrylat; isobornylmethacrylat; hydroxyethylmethacrylat; hydroxypropylmethacrylat; hydroxybutylmethacrylat; benzylmethacrylat; dicyclopentylmethacrylat; tert-butylacrylat; sterylacrylat; 2-phenoxyethylacrylat; tetrahydrofurfurylacrylat; isobornylacrylat; hydroxybutylmethacrylat; benzylacrylat; dicyclopentylacrylat; styren; vinyl toluen; methylstyren; allylglycidylether; acrylamid; methacrylamid; N-methylolacrylamid; N-methylolmethacrylamid; såvel som kombinationer af enhver af ovenstående; og

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2) den multifunktionelle monomer kan udvælges iblandt:

divinylbenzen; allylmethacrylat; allyl cinnimat; ethylenglycoldimethacrylat; diethylenglycoldimethacrylat; triethylenglycoldimethacrylat; dipropylenglycoldimethacrylat; 1,3-butylenglycoldimethacrylat; 1,4-butandioldimethacrylat; 1,6-hexandioldimethacrylat; neopentylglycoldimethacrylat; cyclohexandimethanol-dimethacrylat; dicyclopentyl-dimethacrylat; glyceryltrimethacrylat; trimethylolpropantrimethacrylat; pentaerythritoltrimethacrylat; pentaerythritoltetramethacrylat; dipentaerythritolpentamethacrylat; ethylenglycoldiacrylat; diethylenglycoldiacrylat; triethylenglycoldiacrylat; dipropylenglycoldiacrylat; 1,3-butylenglycoldiacrylat; 1,4-butandioldiacrylat; 1,6-hexandioldiacrylat; neopentylglycoldiacrylat; cyclohexandimethanoldiacrylat; dicyclopentyl-diacrylat; glyceryltriacrylat; trimethylolpropantriacrylat; pentaerythritoltriacrylat; pentaerythritoltetraacrylat; dipentaerythritolpentaacrylat; tris(2-hydroxyethyl)iso-cyanuratriacrylat;

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alkoxyleret versioner af hvilken som helst af de ovennævnte; og metalliske acrylater og methacrylater af zink, magnesium og calcium såvel som kombinationer af enhver af ovenstående.

- 5 6. Sammensætningen ifølge krav 1, hvori den reaktive resin er en ethoxyleret bisphenol A- dimethacrylat.
7. Sammensætningen ifølge krav 1, hvori den funktionelle acetoacetoxymonomer er acetoacetoxyethylmethacrylat.
- 10 8. Sammensætningen ifølge krav 1, hvori silanmonomeren er methacryloxypropyltrimethoxysilan.
9. Sammensætningen ifølge krav 1, hvori dibenzoylperoxiden er phthalat fri.
- 15 10. Sammensætningen ifølge krav 1, hvori den reaktive resin er en ethoxyleret bisphenol A-dimethacrylat; den funktionelle acetoacetoxymonomer er acetoacetoxyethylmethacrylat; silanmonomeren er methacryloxypropyltrimethoxysilan; og dibenzoylperoxiden er phthalat fri.
- 20 11. En hærdelig klæbemiddelssammensætning til fastgøring af elementer i et strukturelt legeme, omfattende:
 - 25 a. mindst en reaktiv resin omfattende en polymeriserbar monomer som indeholder eller inkludere mindst en funktionel gruppe udvalgt iblandt: acrylater; methacrylater; såvel som enhver kombination deraf; i kombination med en phenol udvalgt iblandt; bisphenol A; bisphenol F; bisphenol S; novalak monomerer; og kombinationer deraf.
 - 30 b. mindst en funktionel acetoacetoxymonomer
 - c. mindst en silanmonomer;
 - d. en fri radikal initiator; og
 - e. en accelerator;
 - 35 hvori den frie radikal initiator er dibenzoylperoxid, og acceleratoren er udvalgt fra gruppen bestående af: N,N-diisopropanol-p-toluidin; N,N-dihydroxyethyl-p-toluidin; N,N-methylhydroxyethyl-p-toluidin; og blandinger deraf.