A flooring system includes a plurality of tongue-and-groove panels, and a preglu. When activated, the preglu has a tensile strength of 7-20 kN/m when measured with a gap less than 0.1 mm and a pull rate of 2 mm/min; a storage stability of at least one year; a low initial tack value; and a set time of at least 45 minutes; as well as a creep strength of between 7 and 20 kN/m, when measured with a gap less than 0.1 mm and a pull rate of 0.02 mm/min.
Fig. 1

Monomer + First-part curative

Second-part curative (catalyst)

Second-part curative (activator)
Fig. 2

- △ - Catalyst
- □ - Activator
FLOORING SYSTEM INCLUDING A DRY GLUE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This PCT application claims priority from U.S. Provisional Application No. 60/701,486, filed Jul. 22, 2005.

BACKGROUND

[0002] 1. Field of the Invention

[0003] The invention is a flooring system, utilizing a number of flooring elements, and a “dry” (to the touch) glue for maintaining a tight joint between the flooring elements.

[0004] 2. Background of the Invention

[0005] Wood or laminate flooring has become increasingly popular. As such, many different types of this flooring have been developed. Generally, this type of flooring is assembled by providing a plurality of similar panels, which are interfit or otherwise secured together and which “float” above the subfloor, i.e., the flooring is not mechanically attached to the subfloor.

[0006] In conventional hardwood or other flooring systems, edges of rectangular boards or planks are often provided with a tongue-and-groove joining system, whereby a first plank has on at least one edge, a protruding tongue, and a second plank, to be installed adjacent and abutting the first plank, has, on at least one side, a groove, which corresponds substantially to the size and shape of the tongue. Thus, in order to install the first board adjacent to the second board, the tongue is inserted into the groove. In some systems, the tongue and groove form a lock, hindering or preventing separation of the boards.

[0007] Such conventional tongue-and-groove systems are generally installed by relatively moving one panel with respect to the second panel. For example, U.S. Pat. Nos. 6,421,970 and 6,823,638 teach a system whereby the boards are moved relatively horizontally. U.S. Pat. Nos. 6,591,568 and 6,647,690 teach systems whereby assembly can be completed by rotating and/or through a vertical movement. Other examples of tongue-and-groove systems are disclosed by U.S. Pat. Nos. 6,786,019; 6,906,486; 6,862,861; 6,711,869; 6,536,178 (relative vertical movement); U.S. Pat. No. 6,601,359 (relative horizontal or rotational movement); and U.S. Pat. No. 6,865,855. The resulting joint may also have fitting clearances for the drainage of adhesive, if any, such as described by U.S. Pat. No. 6,682,254. Additional components, such as joining profiles, guiding means or resilient members may also be used, for example as taught by U.S. Pat. Nos. 6,729,091; 6,763,643; 6,966,161; 6,920,732; and 6,854,235. Each of the references mentioned in this paragraph is expressly incorporated by reference in its entirety.

[0008] Additionally, the size and shape of the tongues and grooves varies greatly. For example, U.S. Pat. No. 6,823,638 (herein incorporated by reference in its entirety) teaches a tongue with a groove provided therein and a corresponding groove with a tongue provided therein.

[0009] Typical flooring elements used in accordance with the present invention are laminate flooring elements, including a core, a decorative surface, and a wear layer. Typical cores include wood, fiberboard, such as high density fiberboard (HDF) or medium density fiberboard (MDF), gypsum, high-density reinforced plaster, plywood, oriented strand board (OSB), cork, bamboo, flexboard, plastics (e.g., extrudable and/or moldable thermosetting and thermoplastic resins, the latter including high density olefins and PVC), or other structural material, such as metals (e.g., aluminum, copper, brass, alloys thereof and stainless steel) or composites.

[0010] Such laminate flooring elements generally include a decorative surface. Typical decorative surfaces are formed from one or more patterned paper sheets, impregnated with a resin, and placed atop the core. Many elements also are provided with a surface texture which coincides with the pattern or design of the paper sheets, in order to enhance the realism thereof, as described by U.S. Pat. No. 7,003,364 (herein incorporated by reference in its entirety). However, such decorative surface can be provided by printing directly, on the core material. The uppermost surface of the element most often includes a wear layer, formed by a resinous layer including hard particles to impart resistance against scratching, abrasion, and denting. Such particles are, typically, diamond, silicon carbide, alumina (e.g., alpha-alumina), or ceramics, which can have a Mohs’ hardness of at least 6.0.

[0011] However, in many of these systems, especially floating floors, an adhesive or glue is often used, such that the assembled panels do not separate. Most often, the glue must be separately purchased, and separately applied in a step immediately preceding joining of the panels.

[0012] Although flooring systems have been commercialized with a “preglue,” wherein the glue or other adhesive is applied at the factory, such systems have drawbacks, and have heretofore required an additional step. Such additional steps typically include application of an external agent (e.g., water or other chemical activating agent, and ultrasonic waves—either immediately before or following installation), or removal of a protective strip, in order to render the preglue in its active state.

SUMMARY OF THE INVENTION

[0013] Thus, the present inventors have developed a flooring system using a “dry” preglue system, which preglue is applied at the factory, which does not require a separate application of an external agent or removal of a protective strip, and/or which additionally provides adhesive properties not found in any commercial system.

[0014] In one embodiment, the adhesive or components of the adhesive which react with one more other components can be contained in small “microcapsules,” which, under pressure and/or shear, can be ruptured to allow the glue to adhere to the panels. Examples of “microcapsules” are disclosed in U.S. Publication No. 2002-0127374 (herein incorporated by reference in its entirety), and may be organic or inorganic.

[0015] According to the invention, upon assembly of the panels, and mating of the tongue and groove, the adhesive becomes operative to prevent the panels from separating, by even a small amount. This can be accomplished by rupturing one or more containers, such as the aforementioned microcapsules, containing the glue or precursors thereof. Such containers may also be in the form of one or more tubes containing, e.g., the adhesive material (such as in an encapsulated form therein), separated activators and/or precursors, or two-part systems. Such tubes can be segmented with seals therebetween, such as a described by U.S. Pat. No. 7,029,741, herein incorporated by reference in its entirety.

[0016] In a preferred embodiment, the adhesive, once activated and finally set, will exhibit particular properties. For example, the following properties are preferred.
In one embodiment, the adhesive, or components thereof, is applied to the entire surface of each of the tongue and groove, but more typically, the adhesive is strategically placed in select locations on the tongue and/or inside the groove. By selecting these application locations, the effectiveness of the adhesive can be maximized.

**BRIEF DESCRIPTION OF THE DRAWINGS**

**[0017]** FIG. 1 is a schematic illustrating an embodiment of the invention showing a first-part curative and second-part curative.

**[0018]** FIG. 2 is a cutaway perspective view of a substrate having coatings applied according to an embodiment of the invention.

**[0019]** FIG. 3 is a side view of an alternative embodiment depicting encapsulated activator showing the second-part curative where catalyst is applied as a lower layer, and where activator is separately microencapsulated.

**[0020]** FIG. 4 is an alternative embodiment depicting the second-part curative where activator is a lower layer and catalyst is the middle layer or is in a middle layer.

**[0021]** FIG. 5 is an embodiment depicting the second-part curative disposed on opposite sides of the layer with the microcapsules containing monomer and the first-part curative.

**[0022]** FIG. 6 illustrates alternate embodiments where the components of the system are coated onto separate surfaces. In version A the capsules with first-part curative are applied to the same surface with catalyst. In version B the catalyst is applied to the surface coated with a second population of capsules encapsulating activator.

**[0023]** FIGS. 6 and 7 show a tongue-and-groove system which may be used with the preglue in accordance with the invention.

**[0024]** FIG. 8 shows the tongue-and-groove system of FIG. 6 in its assembled condition.

**[0025]** FIG. 9 shows a second tongue-and-groove system which may be used in accordance with the invention.

**[0026]** FIG. 10 shows an additional tongue-and-groove system which may be used with the preglue in accordance with the invention.

**DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

**[0027]** Initially, as used throughout the specification and claims, the terms “plank,” “board,” and “tile” mean any type of surface covering material and in any shape. For example, the planks, boards and tiles may be part of a flooring, wall covering, desk, countertop, cabinet, door, vehicle or ceiling component, and can be rectangular, square or have the shape of any other polygon. Although the glue of the invention is particularly designed to be used with laminate flooring materials, the terms “plank,” “board” and “tile” are not so limited. For example, board can convey any type of flooring material, including, plastic, composite materials, hardwood, flexboard, high density fiber-reinforced plaster, extruded wood, engineered wood, and even ceramic and other non-cellulosic materials. Additionally, the planks may have a decorative upper surface, formed from a material different from that of the remainder of the plank. Typical materials include, laminates (such as foils, plastic sheets, and ceramics (e.g., individual tiles)).

**[0029]** Similarly, the term “preglue,” “glue” and “adhesive” as used in the specification and claims, means a substance which can chemically or physically join two, at least tangentially, adjacent surfaces to secure the surfaces together. In some cases, such a substance can be applied during manufacture of the panels. That is to say, before the panels leave the factory, the glue is applied, thus eliminating the need to provide a separate adhesive material just before assembly. Typically, the glue is applied in a non-activated state, such that some later event is needed to convert the preglue into its adhesive state. This invention is particularly directed to a dry preglue, i.e., a glue which is applied at the factory, but does not need the application of an external activator to cause the adhesive effect. Such adhesive effect if preferably achieved by breaking or rupturing a film, such as the wall of a microcapsule or segmented tube. It is additionally considered within the scope of the invention to apply the glue in an activated state, but have a suppressing agent applied thereto, such that the glue has been “de-activated,” awaiting “re-activation” at a later time.

**[0030]** FIG. 7 shows a typical tongue-and-groove system which is designed to be assembled horizontally with which the dry preglue of the invention may be used. A first panel 110 is provided with a tongue 112. The tongue 112 is provided with a retaining element 114, and a distal surface 116, as well as an upper surface 118 and a lower surface 120. Additionally, as shown in FIG. 7, the first panel 110 includes a nose 122, designed to abut an adjacent panel when assembled to form a solid, gap-free surface.

**[0031]** A second panel 140 is provided with a groove 141, a cooperating retaining element 142, and a proximal surface 144, as well as upper and lower surfaces, 146 and 148 respectively, and a distal upper surface 150.

**[0032]** Although the retaining elements 114 and 142 are shown as being of a particular construction and at a particular location, such a configuration is shown for convenience only. In other words, the size, shape, type and/or location of the retaining elements 114 and 142 may be altered in any manner without departing from the invention. Thus, the preglue of the invention may be used on any type of tongue-and-groove system known in the art, such as those disclosed in, but not limited to those of, U.S. Pat. No. 6,421,970, No. 6,591,568, No. 6,647,690, and No. 5,823,638 (each of which is hereby incorporated by reference in its entirety). Similarly, there may be multiple retaining elements 114, 142. Moreover, it should be understood that the first panel 110 may be joined to the second panel 140 by, for example, relative horizontal movement, and to a third panel 160 (not shown) by an alternative method, e.g., by relative vertical or rotational movement.

**[0033]** Similarly, as the invention utilizes an adhesive material, it is considered within the scope of the invention to eliminate the retaining elements 114 and 142 entirely, thus relying totally upon the adhesive strength of the preglue.
Additionally, the retaining elements 114, 142 need not be sufficient, alone, to hold the panels 110, 140 together when under normal use.

[0034] For example, as long as the remaining elements 114, 142 can maintain the position of the panels 110, 140 in their installed positions for at least a short period of time, the preglue of the invention can have enough time to set, to maintain a secure connection, such as a tight joint, of the panels 110, 140. In one embodiment, the locking elements 114, 142 can be assembled by human manual pressure, i.e., human muscle power alone, without the need for additional mechanical tools, such as a tapping block and hammer, as is commonly required to assemble locking elements previously known in the art.

[0035] FIG. 8 shows the first panel 110 and the second panel 140 after assembly. Specifically, the tongue 112 of the first panel 110 is inserted into the groove 141 of the second panel to secure the panels 110, 140 together. When assembled, the panels 110, 140 meet at least where the top surface 118 of the tongue 112 meets the upper surface 146, and where the lower surface of the tongue 120 meets the lower surface of the groove 148, as well as where the nose 122 meets the distal upper surface 150. In a preferred embodiment, each of these contact surfaces 20a-d, the preglue of the invention functions to hold the panels 110, 140 together. However, it is within the scope of the invention to apply the preglue to any number of the contact surfaces 20a-d, and in any combination.

[0036] In addition to the horizontally joined panels as shown in FIGS. 7 and 8, the invention is applicable to be used with any assembly method. For example, FIG. 9 depicts a typical tongue-and-groove system which is designed to be assembled vertically with which the preglue of the invention, and FIG. 10 depicts a typical tongue-and-groove system which may be assembled through rotational movement with the preglue of the invention.

[0037] In a preferred embodiment, the dry preglue exhibits specific properties. For example, the creep strength with a gap less than 0.10 mm and a pull rate of 0.02 mm/min is between 1 and 50 kN/m, typically 2-30 kN/m, more typically 7-20 kN/m and preferably 10-15 kN/m. The creep strength can never be too high, and the minimum value is based, in part, on what type of flooring is used. For a typical laminate floor, formed from low or high pressure laminate with a traditional high or medium density fibreboard core, a minimum value should be above 10 kN/m.

[0038] The creep strength is measured with a gap between the laminate edges being less than 0.10 mm, at a strength of 10-15 kN/m. Normally such joint strength is measured at high piston rate, typically 2 mm/min. However, in an installed floor there are long term forces generated from humidity and temperature changes, and over time this can create gaps between the planks. The reason for applying the adhesive is to increase the strength of the joint, so it can resist these long-term forces. Simulating such the slow forces was performed with a uniaxial machine, such as Lloyd LR50K testing machine (available from AMKTEK, Inc., of Largo, Fla.) with an external extensometer, and the pieces were pulled apart with a joint opening rate of 0.02 mm/min. This pull rate is chosen for practical reasons (it is possible to use other pull rates 0.001-1 mm/min) and that it correlates with previous performed long-term strength tests. In long term strength tests, identical test pieces are hanged with different weights. The weight is increased over time, until the test piece breaks. This could take several weeks.

[0039] The preglue of the invention also has a particular tensile strength. For example, the tensile strength with a gap less than 0.10 mm and a pull rate of 2 mm/min is between 1 and 50 kN/m, typically 2-30 kN/m, more typically 7-20 kN/m and preferably 10-15 kN/m. The tensile strength is measured in the same way as the creep strength except for the pull rate (2 mm/min). Here, also the gap is important.

[0040] An important factor in the commercial viability of the preglue is the storage stability after application on planks. In an embodiment, the preglue can maintain its properties for at least 6 months, typically greater than 9 months, and preferably at least as long as one full year, when maintained at a temperature of between 10 and 150°F (-12-66°C), irrespective of the relative humidity. The adhesive typically meets the creep strength requirement after one year of having been applied on the board. Temperature and humidity are the important environmental conditions. The capsules typically also withstand normal light, so it is not necessary to pack the planks with special foil, and should also withstand exposure to oxygen and air without the need for any additional materials, such as coatings or packaging.

[0041] Preferably only non-toxic materials are used. Such non-toxic materials include those materials that are non-hazardous to humans and other animals (both to the skin and mucous membranes), and other, as may be defined by the Occupational Safety & Health Administration of the United States Department of Labor.

[0042] As used herein, non-toxic may also include hypoallergenic materials, i.e., materials which do not cause allergic reactions in humans. These materials have little, if any, reaction, when they come in contact with human skin or otherwise contact the human body.

[0043] The preferred dry preglue has a low initial tack value, which results in little or no adhesion or attraction of dust and other particles. By maintaining a low initial tack value, any negative influence from the presence of dust and other small particles can be significantly reduced if not eliminated. Initial tack, as used throughout this specification and claims, means before the capsules are broken. Such tackiness can be measured via any method, but is typically measured visually. The important thing is that no or little dust or particles adheres to the adhesive before the planks are assembled. The risks with adhesion of dust are that it can be difficult to assemble the planks, create proud edges and the strength of the adhesive can be reduced.

[0044] In one embodiment, the dry preglue has little or no smell, either before or after activation. Such a condition will be tested at the Swedish National Testing and Research Institute (SP). The important thing is that there is no unpleasant smell from the adhesive during installation and after the installation. Smell is difficult to measure because different people react differently to smells. What SP will do is to measure the volatile components with a method called FLEC (field and laboratory emission cell). The presence or absence of smell or odor can also be measured by human observation. However, in other embodiments of the invention, the release or origination of organic or inorganic odiferous components (such as a mercaptan or other sulfur-containing component) can alert the installer that the dry preglue has been activated. In such circumstances, odiferous substances can be readily
identified in minute quantities, e.g., on the order of 100 ppm, 50 ppm or even as low as 10 ppm, could be released or generated.

[0045] Once the dry preglue has been activated, in preferred embodiments, the glue should not begin to set until the expiration of a predetermined period of time. By providing a predetermined set time of, for example, as long as 45 minutes to one hour, the installer is given an opportunity to assemble the planks, and if needed, remove one or more without destroying them. If, for example, one plank was damaged or was not completely interfit with the adjacent panels, the installer would be able to correct this problem. Practical set times can be between 1 minute and 1 hour, typically between 10 and 45 minutes, and preferably between 10 and 15 minutes. Longer predetermined set times force the installer to avoid putting pressure on the joints until after the set time has expired, and shorter set times negate the ability to disassemble the boards without damage thereto.

[0046] Once the preglue begins to set, it should achieve its final properties, such as creep strength and tensile strength within a reasonable curing time. Typical curing times can be as long as one week, but are preferably less than 2 days, and most preferably less than 24 hours.

[0047] The preglue may be applied in any number of manners to the panels. Particular examples of the locations of which the glue may be applied are taught by U.S. Published Application No. 2002-0187747 (incorporated by reference in its entirety), wherein the adhesive is applied to substantially all of each surface of the tongue 112, other than the distal surface 116, as well as to substantially all surfaces of the groove 141, other than the proximal surface 144. Such capsules typically have a diameter between 1 and 700 μm, more typically between 10 and 100 μm, and preferably between 10 and 50 μm.

[0048] While it is preferred that the preglue system be spread across the entire length of the edge of the tongue and/or groove, it is considered within the invention to apply the components on substantially less than the entire edge. For example, depending upon the type of locking element being used, it may only be necessary to have the glue system on, 75%, 50%, 25% or even 10% or less of the entire length of the edge.

[0049] In one embodiment, the preglue system requires (A) a monomer, (B) an initiator, (C) an activator, and (D) a catalyst. In order for the preglue to become fully activated, typically, it is necessary to react each of components (A)-(C) in the presence of (D). Thus, when the panels of the invention leave the factory, at least one component is typically separated from the remainder. Separating can be spatial or can involve isolation of one or more components, such as by microencapsulation.

[0050] Generally, the system additionally typically includes a binder. One or more of the components, preferably the catalyst, may be contained in the binder. Suitable binders are carriers or vehicles for the microcapsules or non-encapsulated component and can include dried solvents. Examples of binder materials include water-based adhesives or lacquers (e.g., PVAc), solvent based adhesives or lacquers, UV-curing adhesives or lacquer, latex, starch, only solvent and only water.

[0051] Other optional components include a foaming agent, such as polyols and polyethers with isocyanates which cause the glue to foam or bubble when activated. By utilizing such a foaming agent, the glue can expand in volume to flow and fill interstices or spaces between the planks. This is especially desirable when it is desired to seal the space between the planks immediately below the noses of the planks.

[0052] The monomer can be any material, which, when exposed one or more other components forms a polymer which can join the boards of the invention. Typical monomers include acrylates, urethanes and epoxies and are preferably 100% solidified and cured by the action of free radicals, cationic reactions and anionic reactions. The catalyst is typically copper, such as a copper solution, e.g., copper chloride in an acetone solvent.

[0053] The initiator is typically a chemical added to help start the chemical reaction such as polymerization, needed to activate or set the adhesive. Such polymerization may be cross-linking or chain extending. Its action is typically similar to that of a catalyst, except that it is usually consumed in the reaction. In polymer chemistry, an initiator is a chemical compound that initiates a chain reaction. Typically these compounds decompose to form either radical, anionic, or cationic species, which in turn serve as a reactive center for the propagation of chain polymerization. An example of a commonly used radical initiator would be tertiary-butyl hydroperoxide. This is a water soluble compound that, upon mild heating, breaks into two radical species. The initiator is typically a peroxide, such as cumene hydroperoxide.

[0054] The activator is typically a chemical used to accelerate a reaction or increase chemical activity in another material, for example, to activate the initiator to begin the reaction. A generic example a suitable activators are amines.

[0055] The adhesive system may be formulated as follows:

[0056] a. Capsule 1:

[0057] i. Monomers (tetrahydrofururyl methacrylate and butylene glycol dimethacrylate) and

[0058] ii. Initiator (cumene hydroperoxide).

[0059] b. Capsule 2:

[0060] i. Activator (propyl dihydroperoxide).

[0061] c. The binder contains the catalyst (copper dichloride dihydrate).

[0062] d. When the capsules are broken, the activator activates the initiator and then the initiator initiates the polymerization of the monomers and the catalyst catalyzes the polymerization reaction.

[0063] The various components, as well as binder therefor, can be applied in a number of manners. Typical examples include, vacuum coating, spraying, rolling, brushing, dipping, and electrostatic spraying. When applied, the wet film thickness is typically less than 500 μm, more typically less than 200 μm, and preferably less than 100 μm. However, after activation, the thickness is typically less than 1000 μm, more typically less than 500 μm, and preferably less than 200 μm.

[0064] The wet film thickness should be less than 1000 μm and, more typically between 300 and 600 μm. The dry film thickness should be less than 800 μm and, typically less than 500 μm, and preferably between 150 and 300 μm. However, after activation, the thickness is typically less than 500 μm, more typically less than 200 μm, and preferably less than 100 μm.

[0065] It is possible to separate the components by applying the components to both of the panels. However, in order to prevent mixing of the components prematurely, at least one of the components must be separated from the remainder. In one embodiment, components (B)-(D) are applied to one of the tongue or groove, and the monomer is applied to the other of the tongue and groove. Thus, when the tongue and groove are
mated, the monomer can contact the activator, catalyst and initiator to activate the glue. Similarly, the components may be separated in any manner, as long as the activation can be prohibited until desired.

[0066] It is also possible to encapsulate one or more of the components. For example, instead of having one or more components, such as the monomer, separated from the remaining components by being located on a separate panel, one or more components can be encapsulated to prevent mixing until desired. This encapsulation may be organic or inorganic, such as that which is disclosed in U.S. Publication No. 2002-0127374, as well as one or more of melamine, urea and formaldehyde. The capsules, regardless of their size, may also be formed from glass, polymer, gelable colloids and other materials as hereinbefore discussed, or another substantially rigid material. In these embodiments, pressure generated by physically joining the boards causes the capsules to rupture.

[0067] In another embodiment, the capsules are broken by a chemical reaction. For example, the capsule can include a material which, when exposed to a solvent located on the opposite board, will rupture or otherwise open, allowing the escape of the contents contained therein.

[0068] In one embodiment, the mixing or contact of the various components causes an additional reaction, giving the user some indication that the components have been contacted and that the glue has become activated. The additional reaction is something that can be observed by the user, and need not have any effect on any other property. Such reactions can be smell, color, temperature, turbidity or cloudiness, or any other observable change.

[0069] The various components may be provided on the boards in a number of manners/locations. For example, as follows.

[0070] a. The components can be separated on the panels, such as components (A)-(C) on one panel and (D) on the second panel. In one embodiment, only the catalyst is provided on the second panel.

[0071] b. One or more components can be encapsulated, and at least one is not encapsulated. In this embodiment, the components are maintained apart by their relative encapsulation, rather than by being provided on different panels. Again, more than one component can be provided in a microcapsule. In one embodiment, components (A), (B) and/or (C) are encapsulated, and (D) is simply applied to the panel. Typically, initiator (B) and activator (C) are not placed in the same capsule. Because the components are inherently separated, the microcapsules and other components all can be provided on one or both boards.

[0072] c. One or more of the components can be integral with the board. In other words, one component, such as the catalyst, may be impregnated into the structure of the panel, either only at the edge, or mixed throughout the panel.

[0073] d. Multiple microcapsules can be used, wherein the components are maintained separated by being provided in separate microcapsules. Typically, the catalyst is provided in its own microcapsule.

[0074] e. A solvent for a microcapsule can be provided in a glass microcapsule. In this embodiment, a solvent for a microcapsule is provided in a glass (or other inert substance which interferes with neither any component nor the final adhesive system) capsule. When the glass capsule is ruptured, typically by physical pressure, the solvent is released, and such solvent is free to act on the microcapsule(s) containing the component(s).

[0075] f. The microcapsule(s) can be ruptured by heat or other external forces. In one embodiment, either immediately before the panels are assembled or sometime after assembly, radiation (such as ultrasonic, heat, microwave, electromagnetic, etc.) is applied to rupture the microcapsule(s).

[0076] The present invention teaches an improved adhesive composition especially suited for forming high strength dry-to-the-touch structural adhesives. The adhesive composition of the invention, in some embodiments, is a thin layer flowable adhesive providing a dry-to-the-touch adhesive providing high strength when joining interference fit components. At least one of the adhesive constituents flows into contact with the other constituents of the adhesive composition to form a high strength structural adhesive.

[0077] In a preferred embodiment a flowable monomer is encapsulated together with initiator, as described by U.S. Provisional Application No. 60/_______, titled Encapsulated Structural Adhesive, filed Jul. 22, 2005 (Atty. Docket No. 6595) in the name of Sandra Jacqueline Guinebretiere et al., herein incorporated by reference in its entirety. A flowable activator can be separately encapsulated or positioned in a binder material, matrix or carrier for the adhesive composition. For convenience herein, all such materials are referred to as binder or binders herein. Upon capsule rupture, the flowable constituents of monomer, initiator and activator flow into reactive contact with each other and a catalyst forming a high strength adhesive.

[0078] The present invention in various embodiments teaches an encapsulated curable adhesive composition comprising a two part curative, e.g., activator and curative. The curative consists substantially of a first-part curative of a preferably peroxo initiator, and a second-part curative. Other additives can also be present such as rheology modifiers, pigments, fragrances, odor-masking agents, fillers, colorants and plasticizers. In one embodiment, a first population of polymeric microcapsules encases the initiator and monomer which is reactive with the second-part curative. The second-part curative is also of two parts or two components. The capsules encase both the first-part curative and the monomer whereby forming a monomer and initiator (first-part curative) blend. The polymeric microcapsules are substantially impermeable to both parts of the curative. The monomer is selected from flowable (meth)acrylate esters, epoxy(meth)acrylate and methacrylate esters. For convenience the term “(meth)acrylate” is to be understood as used herein and in the claims as referring to both the acrylate and methacrylate versions of the specified monomer. However, the encapsulated monomer and initiator blend is a free flowing liquid having a viscosity of less than 500 milliPascal-second (Cp) (Centipoise). The term “monomer” in the specification and claims should be understood as being defined for purposes hereof to include monomers and oligomers thereof and blends of monomers and oligomers provided the requisite viscosity parameters of the resultant blend are met. The monomer preferably has a Tg of 35° C. or less or is blended with monomers to have a resultant Tg of less than 35° C. The second-part curative comprises a catalyst and activator. The second-part curative is preferably external to the polymeric microcapsules containing monomer and initiator disposed on the substrate to be joined, or in a binder or carrier for the
system, or on the outside of the microcapsules. Alternatively, the activator of the second-part curative is separately encapsulated or positioned in a binder material, matrix or carrier for the adhesive composition. The catalyst is typically external to the microcapsules, and can be in the binder or carrier or applied as a first coating to a substrate which is over coated with the balance of the components of the structural adhesive. Optionally, the catalyst may be separately encapsulated or positioned in a binder material, matrix or carrier for the adhesive composition.

[0079] An encapsulated curable adhesive composition is taught for forming high strength structural adhesives. In the majority of embodiments, these structural adhesives are able to be fashioned as dry-to-the-touch coatings before activation.

[0080] The encapsulated curable adhesive composition comprises a two part curative comprised of a first-part curative and a second-part curative. The first-part curative is an initiator material. The second-part curative is a catalyst and an activator. The adhesive composition includes a first population of polymeric microcapsules encapsulating a monomer reactive with the two part curative when “complete,” meaning that the initiator, catalyst and activator have all come together, enabling reactive contact. The internal contents or core of the first population of microcapsules includes a flowable monomer or monomers reactive with the two part curative. Prior to encapsulation, the monomer is blended with the first-part curative forming a blend of the monomer and initiator. This blend of monomer and first-part curative forms the core of the first population of microcapsules. The second-part curative comprises catalyst preferably a water soluble catalyst such as a copper metal salt, and an activator. A binder material is also provided to retain the population of microcapsules and two-part curative in proximity such as when coated on a substrate to be joined. Preferably the activator is separately encapsulated forming a second population of microcapsules.

[0081] The monomer is preferably selected from difunctional acrylates, methacrylate esters, epoxyacrylate esters, epoxycyacrylate, urethane acrylate esters, and melamine acrylate monomers and oligomers. More preferably the monomer is a difunctional methacrylate ester or difunctional urethane acrylate ester. Blends of any of the foregoing are possible.

[0082] Blends of difunctional methacrylate esters together with mono-functional acrylate esters are also particularly useful.

[0083] The monomer and the initiator blend is selected to be a free flowing liquid, meaning a viscosity of less than 500 centipoise. The monomer and initiator blend has a viscosity of less than 500 centipoise (Cp), (at room temperature 25°C unless otherwise indicated). Centipoise is equivalent to milliPascal-second units (milliPascal-second). Viscosity parameters herein are understood as measured at 25°C unless otherwise indicated. Similarly, the activator is preferably separately encapsulated and also selected to be a free flowing liquid.

[0084] Preferably the viscosity of the monomer is less than 100, and even more preferably less than about 7 Cp (milliPascal-second); and the viscosity of the monomer and initiator blend is preferably less than 25 Cp, and more preferably less than 10 Cp.

[0085] Most preferably the viscosity of the monomer and initiator blend is less than 5 Cp (milliPascal-second). A convenient way to measure viscosity is by use of a viscometer such as Brookfield, Model LVF.

[0086] The aspect of achieving a free flowing liquid of the monomer (or monomers) and initiator which forms the internal phase or core of the first population of microcapsules can be accomplished by blending monomers of high viscosity with from 0 to 99 weight percent a lower viscosity monomer. For illustration, melamine acrylate having a viscosity of 1500 Cp can be blended or in essence, diluted, with tetrahydrofuranyl(meth)acrylate and hexanediol dimethacrylate (viscosity<15 Cp) in sufficient weight percent or ratio to achieve a blend with the initiator that is well below 500 Cp (milliPascal-second) making the blend useful as a free flowing liquid in the invention. The useful ratios of such blends to achieve the desirable viscosity of less than 500 Cp can be readily ascertained by the skilled artisan by blending different proportions of viscous and non-viscous monomers.

[0087] Similarly the activator is selected to be a free flowing liquid, and preferably has a viscosity of less than 500 Cp at room temperature, and more preferably less than 100 Cp, and most preferably less than 10 Cp.

[0088] The monomer or blend of monomers is selected to have a Tg of 35°C or less, more preferably less than 25°C, and most preferably less than 10°C. In certain applications a Tg of 1°C or less is similar. Similar to the technique for blending high viscosity monomers with lower viscosity monomers, blending of high Tg monomers with lower Tg monomers can also be done to achieve a resultant Tg for the monomer blend of 35°C or less. Table 1 lists a variety of monomers along with their Tg values and viscosity. Table 1 lists a variety of monomers available from commercial suppliers such as Sartomer (Exton, Pa.) and others. Various monomers and oligomers are available commercially that either have the requisite viscosity and Tg values, or which can be blended together to achieve the requisite viscosity and Tg.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Tg°C</th>
<th>Mw</th>
<th>viscosity Cps</th>
<th>25°C, or</th>
<th>milliPascal-second</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-phenoxoethyl acrylate</td>
<td>5</td>
<td>192</td>
<td>12</td>
<td>2</td>
<td>3000@60°C</td>
</tr>
<tr>
<td>tridecyl acrylate</td>
<td>−55</td>
<td>255</td>
<td>2</td>
<td>37</td>
<td>9975@60°C</td>
</tr>
<tr>
<td>difunctional aliphatic urethane acrylate</td>
<td>−37</td>
<td>660</td>
<td>1.6 hexanediol diacrylate (4) bisphenol diacrylate</td>
<td>43</td>
<td>512</td>
</tr>
</tbody>
</table>

Table 1
### Table 1—continued

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Tg (°C)</th>
<th>Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>caprolactone acrylate</td>
<td>-53</td>
<td>344</td>
</tr>
<tr>
<td>urethane dimethacrylate</td>
<td>25</td>
<td>1740 @ 60°C</td>
</tr>
<tr>
<td>trimethylolpropane trimethacrylate</td>
<td>27</td>
<td>338</td>
</tr>
<tr>
<td>tetrahydrofurfuryl methylacrylate</td>
<td>23</td>
<td>170</td>
</tr>
<tr>
<td>tetrahydrofurfuryl acrylate</td>
<td>-15</td>
<td>156</td>
</tr>
<tr>
<td>tripropylene glycol diacrylate</td>
<td>62</td>
<td>300</td>
</tr>
<tr>
<td>1,6 hexanediol dimethacrylate</td>
<td>30</td>
<td>254</td>
</tr>
<tr>
<td>polyethylene glycol diacrylate</td>
<td>330</td>
<td>15</td>
</tr>
<tr>
<td>1,3 butylene glycol dimethacrylate</td>
<td>29</td>
<td>226</td>
</tr>
<tr>
<td>ethoxylated (2) bisphenol A dimethacrylate</td>
<td>-1</td>
<td>808</td>
</tr>
<tr>
<td>ethoxylated (10) bisphenol A dimethacrylate</td>
<td>-1</td>
<td>808</td>
</tr>
<tr>
<td>caprolactone modified acrylate/glycol hydroxypropionate diacrylate</td>
<td>768</td>
<td>200-300</td>
</tr>
<tr>
<td>melamine acrylate</td>
<td>1500</td>
<td></td>
</tr>
<tr>
<td>aromatic polyester urethane diacrylate oligomer</td>
<td>-40</td>
<td>3195 @ 60°C</td>
</tr>
<tr>
<td>TMPTA trimethylolpropane triacrylate</td>
<td>62</td>
<td>286</td>
</tr>
<tr>
<td>isodecyl acrylate</td>
<td>-60</td>
<td>212</td>
</tr>
<tr>
<td>caprolactone acrylate</td>
<td>-53</td>
<td>344</td>
</tr>
<tr>
<td>ethoxylated bisphenol A diacrylate</td>
<td>60</td>
<td>512</td>
</tr>
<tr>
<td>pentaerythritol tetraacrylate</td>
<td>103</td>
<td>298</td>
</tr>
<tr>
<td>ethoxylated trimethylolpropane triacrylate</td>
<td>103</td>
<td>428</td>
</tr>
<tr>
<td>polypropylene glycol monomethacrylate</td>
<td>405</td>
<td>35</td>
</tr>
<tr>
<td>propoxylated trimethylolpropane triacrylate</td>
<td>-15</td>
<td>470</td>
</tr>
<tr>
<td>propylbutadiene dimethacrylate 80%Hexane/Diol DiAcrylate ester</td>
<td>-75</td>
<td>890 @ 60°C</td>
</tr>
<tr>
<td>20% low viscosity polyester acrylate oligomer</td>
<td>1</td>
<td>630</td>
</tr>
<tr>
<td>polyester acrylate oligomer</td>
<td>21</td>
<td>7700</td>
</tr>
<tr>
<td>epoxy acrylate oligomer</td>
<td>62</td>
<td>250 @ 60°C</td>
</tr>
<tr>
<td>polyester acrylate oligomer</td>
<td>-19</td>
<td>28</td>
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<tr>
<td>polyester acrylate oligomer</td>
<td>42</td>
<td>65</td>
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<tr>
<td>polyester acrylate oligomer</td>
<td>-45</td>
<td>150</td>
</tr>
<tr>
<td>polyester acrylate oligomer</td>
<td>-22</td>
<td>180</td>
</tr>
<tr>
<td>bisphenol A base epoxy acrylate</td>
<td>60</td>
<td>2150 @ 65°C</td>
</tr>
<tr>
<td>epoxy acrylate blended with SR351</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td>aromatic urethane acrylate</td>
<td>50</td>
<td>700 @ 60°C</td>
</tr>
<tr>
<td>aliphatic urethane acrylate</td>
<td>27</td>
<td>660 @ 60°C</td>
</tr>
<tr>
<td>urethane acrylate</td>
<td>-47</td>
<td>4155 @ 60°C</td>
</tr>
<tr>
<td>low viscosity diacrylate oligomer</td>
<td>26</td>
<td>1000</td>
</tr>
<tr>
<td>aliphatic polyester base urethane diacrylate</td>
<td>-38</td>
<td>5825 @ 60°C</td>
</tr>
<tr>
<td>polybutadiene dimethacrylate</td>
<td>-39</td>
<td>4125 @ 60°C</td>
</tr>
<tr>
<td>aliphatic urethane acrylate</td>
<td>30</td>
<td>60000 @ 60°C</td>
</tr>
<tr>
<td>methacrylated polybutadiene</td>
<td>6000</td>
<td>65000 @ 45°C</td>
</tr>
<tr>
<td>methacrylated polybutadiene, UV curable resin, soluble in water</td>
<td>3200</td>
<td>25000</td>
</tr>
<tr>
<td>epoxidized soy bean oil acrylate</td>
<td>-22</td>
<td>25100</td>
</tr>
<tr>
<td>trifunctional urethane acrylate</td>
<td>43</td>
<td>156000</td>
</tr>
<tr>
<td>aromatic urethane acrylate</td>
<td>30</td>
<td>15000 @ 60°C</td>
</tr>
<tr>
<td>aromatic polyester based urethane diacrylate</td>
<td>-20</td>
<td>8000</td>
</tr>
<tr>
<td>polyester acrylate oligomer, water soluble for UV wood coating</td>
<td>20</td>
<td>52000</td>
</tr>
<tr>
<td>polyester acrylate oligomer</td>
<td>35</td>
<td>85000</td>
</tr>
<tr>
<td>aromatic urethane acrylate</td>
<td>35</td>
<td>58000</td>
</tr>
<tr>
<td>aliphatic urethane acrylate</td>
<td>22</td>
<td>6195 @ 60°C</td>
</tr>
<tr>
<td>polybutadiene dimethacrylate 80%/HIDODA 20%</td>
<td>-75</td>
<td>890 @ 60°C</td>
</tr>
<tr>
<td>polyester acrylate oligomer</td>
<td>21</td>
<td>7700</td>
</tr>
<tr>
<td>epoxy acrylate oligomer</td>
<td>62</td>
<td>250 @ 60°C</td>
</tr>
<tr>
<td>polyester acrylate oligomer</td>
<td>42</td>
<td>65</td>
</tr>
<tr>
<td>aromatic urethane acrylate</td>
<td>50</td>
<td>700 @ 60°C</td>
</tr>
<tr>
<td>urethane acrylate</td>
<td>-47</td>
<td>4155 @ 60°C</td>
</tr>
<tr>
<td>caprolactone modified acrylate/glycol hydroxypropionate diacrylate</td>
<td>768</td>
<td>200-300</td>
</tr>
<tr>
<td>urethane diacrylate</td>
<td>25</td>
<td>1740 @ 60°C</td>
</tr>
<tr>
<td>melamine acrylate</td>
<td>25</td>
<td>1740 @ 60°C</td>
</tr>
<tr>
<td>bisphenol A base epoxy acrylate</td>
<td>60</td>
<td>2150 @ 65°C</td>
</tr>
<tr>
<td>urethane dimethacrylate</td>
<td>25</td>
<td>1740 @ 60°C</td>
</tr>
<tr>
<td>caprolactone modified acrylate/glycol hydroxypropionate diacrylate</td>
<td>768</td>
<td>200-300</td>
</tr>
</tbody>
</table>
TABLE 1-continued

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Tg °C</th>
<th>Mw</th>
</tr>
</thead>
<tbody>
<tr>
<td>polybutadiene dimethacrylate 80%/HexaneDiol Diacrylate ester 20%</td>
<td>-75</td>
<td>800@60 C.</td>
</tr>
<tr>
<td>polyester acrylate oligomer</td>
<td>21</td>
<td>7700</td>
</tr>
<tr>
<td>epoxy acrylate oligomer</td>
<td>62</td>
<td>250@60 C.</td>
</tr>
<tr>
<td>polyester acrylate oligomer</td>
<td>42</td>
<td>65</td>
</tr>
<tr>
<td>bisphenol A base epoxy acrylate</td>
<td>60</td>
<td>2150@65 C.</td>
</tr>
<tr>
<td>aromatic urethane acrylate</td>
<td>50</td>
<td>700@60 C.</td>
</tr>
<tr>
<td>urethane acrylate</td>
<td>-47</td>
<td>4155@60</td>
</tr>
</tbody>
</table>

[0089] Viscosity of the internal phase of the capsules is adjustable by blending monomers. In this table the internal phase contains: activator DPC 3% by weight in the monomers or initiator CHP 5% by weight in the monomers, M corresponds to THFA/HDDMA 50/50.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Viscosity (cps, 25°C)</th>
<th>Brookfield model LVE spin 2, 60 rpm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melamine acrylate oligomer (Doreesco UV75° C., 1500 cps)/M 50/50</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Bisphenol A base epoxy acrylate (CN120, 2150 cps @ 65° C)/M 40/60</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Urethane dimethacrylate (CN1963, 1740 cps @ 65° C)/M 50/50</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>Polybutadiene (Ricon 130, 750 cps)/M 50/50</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

[0090] The viscosity of the internal phase is preferably lower than 100 cps. CN120 and CN1963 are products of Sartomer (Exton, Pa.). Doreesco™ is a trademark of Lubrizol, Wickliffe, Ohio. DPC is diphenyl carbazole. CHP is cumene hydroperoxide. M corresponds to tetrahydrofurfural methacrylate (THFA) blended with hexane diol dimethacrylate (HDDMA) in a 50/50 percent ratio by weight.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Activator + diluent monofunctional + difunctional monomer</th>
<th>Resultant Viscosity</th>
<th>Resultant Tg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexanediol dimethacrylate + tetrahydrofurfural methacrylate and 3,5,1,2-dihydro-1-phenyl-2-pyropyrpyridine</td>
<td>&lt;500 Cp</td>
<td>&lt;35 °C.</td>
<td></td>
</tr>
</tbody>
</table>

[0091] Table 3 is another example of blending of monomers to achieve a resultant viscosity of less than 500 Cp and resultant Tg of less than 35 °C.

[0092] The monomer and initiator blend is a free flowing liquid which is encapsulated and comes into reactive contact with both parts of the two-part curative when the capsules are fractured.

[0093] Reactive contact of the monomer and first-part curative with the second-part curative is effected by fracturing, shearing, crushing, or otherwise breaking or degrading the microcapsules so that the free flowing monomer and first-part curative comes into contact with the second-part curative. Mixing occurs through flow of the free flowing monomer and initiator from the capsule interior and flow of activator from the capsule interior upon application of pressure or relative movement of the substrates such as when an interference fit is affected. Common interference fit assemblies include threads on bolts, mortise and tenon, and various snap-fit assemblies or tongue and groove assemblies and couplers.

[0094] The monomers useful in the invention are difunctional acrylate esters, difunctional methacrylate esters and difunctional polyurethane acrylate esters and epoxy acrylates stable in the presence of initiator. Monomers shall be understood as including oligomers thereof. Optionally, an inhibitor such as hydroquinone can be added to the monomer and initiator blend in the capsules to prevent premature polymerization.

[0095] The initiator (first-part of the two-part curative) is blended with the monomer and preferably forms the internal or core contents of the first population of polymeric microcapsules. Optionally the initiator can be separately encapsulated though the preferred embodiment herein is a blending of the monomer and initiator and encapsulation of the blend.

[0096] Useful monomers in the invention are di- and polyfunctional acrylate esters, difunctional (meth)acrylate esters, polyfunctional (meth)acrylate esters, difunctional urethane acrylate esters, polyfunctional urethane acrylate esters and polyfunctional and difunctional epoxy acrylate monomers and oligomers used alone or in combination as blends. In alternate embodiments, optionally, the di- and polyfunctional acrylates, methacrylates, urethane acrylates, and epoxy acrylates are further blended with monofunctional acrylates, methacrylates, urethane acrylates and epoxy acrylates.

[0097] In one form of the embodiment, the encapsulated curable adhesive composition is assembled as a two part system. The curative is of two parts. The first-part curative is a free radical initiator, preferably a peroxy initiator. The initiator is preferably encapsulated together with the monomer. Alternatively the initiator may be separately encapsulated.

[0098] A typical and preferred example of the initiator is cumene hydroperoxide. More particularly, the free radical initiator needs to be soluble or dispersible in the monomers and oligomers. The free radical initiator can be selected from the group of initiators comprising an azo initiator, peroxide, dialkyl peroxide, alkyld peroxide, peroxyster, peroxycarbonate, peroxyketone and peroxydi carbonate. The free radical initiator can be selected from 2,2'-azobisisobutyl nitrite, 2,2'-azobis(2,4-dimethylpentanenitrile), 2,2'-azobis (2,4 dimethylvaleronitrile), 2,2'-azobis(2-methylpropanenitrile), 2,2'-azobis(methylbutyronitrile), 1,1'-azobis(cyclohexanecarbonitrile), 1,1'-azobisisocyanocyclohexane, benzoyl peroxide, decanoyl peroxide; lauroyl peroxide; benzoyl peroxide, di(n-propyl) peroxydicarbonate, di(sec-butyl) peroxydicarbonate, di(2-ethylhexyl)peroxydicarbonate, 1,1'-dimethyl-3-hydroxybutyl peroxyneodecanoate, α-cumyl peroxyneodecanoate, α-amy l peroxyneodecanoate, 1-butyl...
peroxyneodecanoate, t-amyl peroxypivalate, t-butyl peroxypivalate, 2,5-dimethyl 2,5-di(2-ethylhexanoyl peroxide)hexane, t-amyl peroxy-2-ethylhexanoate, t-butyl peroxy-2-ethylhexanoate, t-butyl peroxyacetate, di-t-amyl peroxyacetate, t-butyl peroxide, di-t-amyl peroxide, 2,5-dimethyl-2,5-di(t-butyleroxy)hexane-3, cumene hydroperoxide, 1,1-di(t-butylperoxy)-3,5-trimethyl-cyclohexane, 1,1-di(t-butyleroxy)-cyclohexane, 1,1-di(t-amylperoxy)-cyclohexane, ethyl-3,3-di(t-butylperoxy)-butyrate, t-amyl perbenzoxate, t-butyl perbenzoxate and ethyl 3,3-di(t-amylperoxy)-butyrate.

The initiator is employed at an amount of 10 percent or less by weight in the core of the capsules and more preferably from about 3 to 5 percent by weight, and most preferably 0.1 to 5 percent by weight (based on weight of the internal phase or core of the capsules).

The monomers desirably crosslink in contact with both parts of the two part adhesive. Preferably, the first-part curative is blended with the monomer and encapsulated together with the monomer forming a first population of microcapsules. In one embodiment the second-part curative is positioned external to the microcapsules, for example, on the outside of the capsule wall, on a substrate to be joined, in a carrier, or a binder, with all such placements of the second curative being deemed external to the first population polymeric capsules. The second curative could also be separately encapsulated forming a second population of microcapsules.

The monomers for example can be selected from the group of monomers and oligomers consisting of: alkene glycol dimethacrylate, alkyl dimethacrylate, alkylidio dimethacrylate, alkoxyl alkanol diacrylate, trialkanol triacylate, alkoxylalkoxy(alkoxy), alkyl(triacrylate), alkoxylalkoxy(alkoxy), alkyl(dimethacrylate), alkoxyl(dimethacrylate), cycoalkyl(dimethacrylate), bicycloalkyl(dimethacrylate), cycloalkoxy(dimethacrylate), cycloalkoxy(dimethacrylate), alkene glycol diacrylate, alkyl diacrylate, alkylidio diacrylate, alkoxylalkanol dimethacrylate, trialkanol trimethacrylate, alkoxylalkoxy(alkoxy), alkyl trimehacrylate, alkoxylalkoxy(alkoxy), alkyl dialcylacrylate, cycloalkyl dialcylacrylate, cycloalkoxy dialcylacrylate, wherein the alkyl and alkene moieties are of 1 to 16 carbons, the cycoalkyl moieties are of 4 to 8 carbons, and n is an integer from 1 to 6. Aromatic polyether urethane(meth)acrylates, aliphatic polyester, aliphatic urethane acrylate including alkyl, alkenyl or aryl substituted or unsubstituted urethane acrylates and epoxy acrylates can also be advantageously employed.

More specifically, by way of illustration and not limitation, the monomers can be selected from any of hexyl dimethacrylate; triethylene glycol dimethacrylate; ethylene glycol dimethacrylate; tetraethylene glycol dimethacrylate; polyethylene glycol dimethacrylate; 1,3 butylene glycol diacrylate; 1,4-butanediol dimethacrylate; 1,4-butanediol diacrylate; diethylene glycol diacrylate; diethylene glycol dimethacrylate; 1,6 hexanediol diacrylate; 1,6 hexanediol dimethacrylate; neopentyl glycol diacrylate; neopentyl glycol dimethacrylate; polyethylene glycol diacrylate; triethylene glycol diacrylate; triethylene glycol di acidrate; 1,3 butylene glycol dimethacrylate; tripropylene glycol diacrylate; ethoxylated bisphenol diacrylate; ethoxylated bisphenol dimethacrylate; diethylene glycol diacrylate; 1,3 butylene glycol dimethacrylate; 1,6 hexanediol diacrylate; 1,6 hexanediol dimethacrylate; propoxylated neopentyl glycol diacrylate; trimethylolpropane trimethacrylate; trimethylolpropane triacylate; pentaerythritol triacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated trimethylolpropane triacrylate, propoxylated glycerol triacrylate, diterthylolpropane tetaacrylate, dipentaerythritol pentaacrylate, ethoxylated pentaerythritol tetaacrylate, and the like, and mixtures thereof.

More particularly, the monofunctional acrylates, methacrylates and urethane acrylates, urethane methacrylates for blending with the monomer include, by way of illustration and not limitation, monomers and oligomers of alkyl acrylate, alkyl acrylate, cycloalkyl acrylate, alkoxy acrylate, cycloalkoxy acrylate, bicycloalkyl acrylate, alkoxyalkoxyacrylate, acrylate, alkyl methacrylate, polyalkylene(meth)acrylate, aralkyl methacrylate, cycloalkyl methacrylate, alkoxy methacrylate, bicycloalkyl methacrylate, cycloalkoxy methacrylate, and alkoxy (alkoxy) methacrylate. The alkyl moieties should be selected preferably of 1 to 16 carbons, the cycloalkyl moieties from 4 to 8 carbons, and n is an integer from 1 to 6.

More particularly the monofunctional acrylates, methacrylate or urethane acrylates or methacrylates can be selected from n-pentyl acrylate, 2-methyl butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate, n-decyl acrylate, n-dodecyl acrylate, lauryl methacrylate, lauryl acrylate, 2-ethylhexyl methacrylate, n-octyl methacrylate, iso-octyl acrylate, iso-octyl methacrylate, isononyl acrylate, isodecyl acrylate, 2-ethoxyethyl methacrylate; butyl diglycol meth acrylate; tetrahydrofurfuryl acrylate; tetrahydrofurfuryl methacrylate; furfuryl methacrylate 2-phenoxypentyl acrylate, isodecyl acrylate; tridecyl acrylate; tridecyl methacrylate; ethoxylated nonyl phenol acrylate and the like and mixtures thereof.

The catalyst is an organic acid or a salt of a transition metal or a metal ion. The catalyst optionally can be separately encapsulated. Preferred are copper salts such as copper chloride. Organo copper salts can also be advantageously employed such as copper acetyl acetone and copper ethyl hexanoate. Optionally the catalyst such as copper salts can be encapsulated with the activator, or optionally even separately encapsulated.

The catalyst is used at about less than 2 percent and more preferably 0.2 to 1 wt percent (based on weight of the reactive constituents making up the adhesive).

An activator, preferably separately encapsulated is included. Useful activators to be used in combination with the catalyst and first population of microcapsules include ferrocene, butyl ferrocene, diethylferrocene, amino rhodanine, diphenyl carbazone, diphenyl carbazidize, dithizone, guaiazu- lene.

More particularly, the activator is an organonitrogen compound such as tertiary amine, amide and imide compounds, aliphatic amines, aldehyde amines, aromatic amines. Specific examples include, without limitation, acetylphenyl hydrazine, diphenyl carbazidize, diphenyl carbazide, dithizone, propyl dihydropropyridine, acetaldehyde-benzylamine, butylaldehydehydniline, benzyamine, various dialkyl amines such as dialkylamine, aniline, toluidine, hexamethylene tetramine, polyethylenemine, aninorhodamine, tetramethylithione, mercaptobenzothiazole, and the like.

The activators are used at preferably less than 10 percent by weight, and more preferably from 1 to 5 percent by weight of the reactive adhesive composition (excluding weight of binder and wall material).
Microcapsules are obtained by providing an aqueous mixture containing a colloidal dispersion of hydrophilic wall-forming material and monomers with initiator.

High shear agitation is applied to the aqueous mixture to achieve a particle size of the core material of about 0.1 to 250 µm (250 microns), preferably 0.1 to 100 microns and more preferably 0.1 to 50 microns. Smaller capsules of 10 µm or less can be produced for specialized applications.

Common microencapsulation processes can be viewed as a series of steps. First, the core material which is to be encapsulated is emulsified or dispersed in a suitable dispersion medium. This medium is preferably aqueous but involves the formation of a polymer rich phase. Most frequently, this medium is a solution of the intended capsule wall material. The solvent characteristics of the medium are changed such as to cause phase separation of the wall material. The wall material is thereby contained in a liquid phase which is also dispersed in the same medium as the intended capsule core material. The liquid wall material phase deposits itself as a continuous coating about the dispersed droplets of the internal phase or capsule core material. The wall material is then solidified. This process is commonly known as coacervation.

Gelatin or gelatin-containing microcapsule wall material is well known. The teachings of the phase separation processes, or coacervation processes which are described in U.S. Pat. Nos. 2,800,457 and 2,800,458 are incorporated herein by reference. Uses of such capsules are described in U.S. Pat. No. 2,730,456.

In situ polymerization, microcapsule walls are formed from materials present in a discontinuous phase. Thus, the wall forming materials dispersed into the discontinuous phase polymerize and migrate outward to the interface between the discontinuous and continuous phases, resulting in the formation of microcapsule wall. Known techniques of in situ polymerization include free radical polymerization and the incorporation of reactive polysacrylates and polyol compounds within the discontinuous phase.

More recent processes of microencapsulation involve, and preferred herein, are the polymerization of urea and formaldehyde, monomer or low molecular weight polymers of dimethylol urea or methylolated dimethylol urea, melamine and formaldehyde, monomer or low molecular weight polymers of methylol melamine or methylated mel- tol melamine, as taught in U.S. Pat. No. 4,552,811 incorporated herein by reference. These materials are dispersed in an aqueous vehicle and the reaction is conducted in the presence of acrylic acid-alkyl acrylate copolymers. The microcapsule can be formed from materials comprising gelable colloids, carboxymethyl cellulose, gelatin, gelatin-gum arabic, methylolated methylol melamine resin, melamine formaldehyde, dimethylol urea, urea formaldehyde, methylol melamine, methylated dimethyl urea, a gelatin anionic polymer, alkyl acrylate-acrylic acid copolymer or other commonly-used polymeric materials used in coacervation.

The invention is not limited to one manner of microencapsulation. Processes of microencapsulation are now well known in the art. U.S. Pat. Nos. 2,730,456, 2,800, 457 and 2,800,458 describe methods for capsule formation. Other useful methods for microcapsule manufacture are: U.S. Pat. Nos. 4,001,140; 4,081,376 and 4,089,802 describing a reaction between urea and formaldehyde; U.S. Pat. No. 4,100,103 describing reaction between melamine and formaldehyde; British Pat. No. 2,062,570 describing a process for producing microcapsules having walls produced by polymerization of melamine and formaldehyde in the presence of a styrene sulfoinic acid. Microcapsules are also taught in U.S. Pat Nos. 2,730,457 and 4,197,346. The more preferred process for forming microcapsules are from urea-formaldehyde resin and/or melamine formaldehyde resin as disclosed in U.S. Pat. Nos. 4,001,140; 4,081,376, 4,089,802; 4,100,103; 4,105,823; 4,444,699 or most preferably alkyl acrylate-acrylic acid copolymer capsules as taught in U.S. Pat. No. 4,552,811. Each patent described is incorporated herein by reference to the extent each provides guidance regarding microencapsulation processes and materials.

Preferably the capsules employed are from 0.1 to 100 microns, preferably 1 to 50 microns, more preferably less than 40, and most preferably less than 30 microns. Other sizes are possible for specific applications.

The first step in the encapsulation process is the preparation of the discrete droplets or domains of the monomer in the dispersion medium. Preferably the initiator is blended first with the monomer. Where such materials are in solution or liquid form and the encapsulation is to be by way of, e.g., coacervation, interfacial polymerization, etc., the dispersion medium solution or liquid containing the monomer and initiator is subjected to high shear mixing or agitation to create a suspension, emulsion or colloidal system of discrete domains of the monomers and initiator blend of the requisite size. The catalyst of the second-part curative can be incorporated into a solid binder or substantially solid carrier, and the carrier or binder may be ground and sorted to a desired particle size. A film forming binder or carrier is preferred through solvated solubilized solids can also be employed. The activator of the second-part curative is preferably in separate microcapsules.

A useful microencapsulation technique is coacervation wherein the material to be encapsulated (monomer and first-part curative) is dispersed or emulsified in a liquid solution of the material to be used as the wall material. The solution is perturbed to cause a phase separation of the wall material, or at least a portion thereof, from the solvent with all or some of the wall material coating the dispersed material to be encapsulated. In this process, the wall forming material may directly separate out onto the emulsified or dispersed core material or it may form its own emulsion with the droplets of the wall material subsequently depositing on the droplets of the core material. In either case, the liquid wall material deposits itself as a continuous coating about the dispersed droplets of the internal phase or capsule core material of monomers and initiator and the wall material is then solidified. Solution perturbation can be any that affects the solubility of the wall material including changes in temperature and addition of another solvent, including, for example, the addition of a non-solvent for the wall material. It should be readily understood by those skilled in the art that the foregoing may be accompanied by a pH shift with wall materials such as gelatin to promote the phase separation in the wall formation step, as taught in Green (U.S. Pat. Nos 2,800,457 and 2,800, 458, incorporated herein by reference).

In coacervation encapsulation, the material to be coated is typically a liquid and is emulsified in the solvent to form droplets which are then coated with the wall material. Sometimes it is advantageous to also employ an emulsification agent to assist with the emulsification of the carrier materials or precursors thereof. Preferred emulsification agents that can be used are amphotrophic; that is, they contain...
both hydrophilic and hydrophobic groups in the same molecule. Exemplary emulsification agents include, but are not limited to, partially hydrolyzed polyvinyl alcohol, starch derivatives, cellulose derivatives, polyacrylamide, and the like. A preferred emulsification agent for use in the invention is partially hydrolyzed polyvinyl alcohol or polyacrylic acid. Polyacrylic acid used as a stabilizer with polyamide wall material was particularly preferable. In a preferred method, high shear agitation is provided to the aqueous mixture to achieve a droplet size of less than about 250 microns, preferably less than 100 microns.

[0121] The conditions for encapsulation will vary based upon the choice of the material used for the capsule wall. Suitable materials for the capsule walls include natural materials such as gelatin, gum arabic, starches, shellacs, and rosin, polymers such as polyvinyl alcohol, polyethylene, polypropylene, polystyrene, polyacrylamides, polyethers, polyesters, polyamides, polybutadiene, polysiloxanes, silicones, epoxies, polyurethanes, formaldehyde resins such as reaction products of formaldehyde with phenols, urea, and melamine, and copolymers such as polyurethane copolymers. Alkylacrylate-acrylic acid copolymer is a preferred wall material.

[0122] Dyestuffs, fillers, plasticizers, binding agents, and other additives can be incorporated in the microcapsule wall or applied to the microcapsule wall surface. One important parameter to keep in mind when formulating wall materials is permeability. Generally, the wall material should have low permeability, at least with respect to the material to be encapsulated. No or low permeability of the capsule wall is particularly important with respect to the second-part curative in the binder or external to the capsules so as to prevent loss of the curative and premature polymerization of the curable composition. Likewise, it may be important for the microcapsule wall to be impermeable or of low permeability to the curable component of the curable composition so as to prevent any ingress of the same or external materials. Dependent upon the encapsulated material, it may also be desirable to formulate the wall material to have low permeability to certain gases such as oxygen or low permeability to liquids such as water or solvents such as toluene or tetrahydrofuran. The requisite permeation rates will vary for each system, but can be met by judicious choice of the wall material and by degree of crosslinking of the wall material. Generally, as crosslinking increases, the permeation rate decreases.

[0123] The microcapsule walls may comprise less than 15 percent and preferably from 5 to 10 percent by weight of the encapsulated components.

[0124] Optionally the microcapsules with monomer and first-part curative, and the second-part curative metal catalyst are dispersed in a binder or adhered to a surface by the binder. The second-part curative activator is separately microencapsulated and also dispersed in the binder or adhered to a surface by the binder. It is to be understood in this context that there are two populations of microcapsules. The first population of microcapsules includes the first-part curative (initiator) with monomer as the capsule core contents. The second-part curative comprises catalyst external to the microcapsules and a second population of microcapsules with activator, preferably a hydrophobic activator. The binder could constitute a carrier material for the capsules. Preferably the binder is a polymeric material or selected from almost any adherent material and preferably selected from binder materials such as polyvinyl alcohol, starches, modified starches, gelatin, hydroxyl ethylcellulose, methyl cellulose, methyl-hydroxypropyl cellulose, or selected from many film forming materials such as carboxylated polyvinyl alcohols, polyacrylates, urethanes, polyvinylacetates, vinyl acetate ethylene copolymers, carboxylated vinyl acetate, polystyrene, or various film forming latexes. The binder is preferably used in an amount sufficient to hold the adhesive constituents or capsules onto the substrate but less than an amount that would interfere with adhesion of the formed adhesive when the capsules are ruptured and the contents come into reactive contact.

[0125] Various additives such as rheology modifiers, rheology aids, tackifiers, plasticizers, rubberized particles, styrene-butadiene rubber lattices, lubricants, toners, coloring agents, can be optionally employed.

[0126] Optionally, as an alternative embodiment the binder material can be selected to be UV curable binders include materials such as those curable using electron beam, UV radiation or visible light, such as acrylated monomers or oligomers of acrylated epoxy resins, acrylated urethanes and polyester acrylates and acrylated monomers including monoacrylated, multiacrylated monomers, and thermally curable resins such as phenolic resins, urea/formaldehyde resins and epoxy resins, as well as mixtures of such resins. The curing mechanism through UV light can be employed with or without the assistance of an additional thermal cure mechanism. In the context of this application it is understood that the term “radiation curable” embraces the use of visible light, or ultraviolet (UV) light, and electron functions and radiation cure functions can be provided by different functionalities in the same molecule.

[0127] If UV cure of the binder is desired, generally any UV-curable binder may be chosen. Examples of suitable binders also include unsaturated polyester resin and alkyl resins, unsaturated melamine formaldehyde resins, polybutadiene resins, and unsaturated compounds such as (meth)acrylates and allyl compounds.

[0128] Examples of UV-curable polyesters include polycondensation products from unsaturated di- or polycarboxylic acids or derivatives thereof; for instance: maleic acid, maleic anhydride and/or fumaric acid, and polyols such as ethylene glycol, 1,2-propane diol, diethylene glycol, hexane diol, glycerol, trimethylol propane or pentaerythritol. These polyesters can be blended with ethynically unsaturated nonmoneric compounds, such as methacryl compounds and vinyl compounds, including acrylate compounds and allyl compounds.

[0129] Illustrative UV curable (meth)acrylates and allyl compounds include methyl acrylate, methyl methacrylate, ethyl acrylate, ethyl methacrylate, butyl acrylate; (meth)acrylic esters of aliphatic diols and/or polyols, for instance: ethylene diacrylate, trimethylol propane triacrylate and pentaerythritol tetraacrylate; hydroxyl(meth)acrylates such as hydroxethyl acrylate, 2-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, 4-hydroxybutyl acrylate and pentaerythritol triacrylate and allyl compounds such as diallyl phthalate, diallyl maleate, triallyl isocyanurate and ethylene glycol diallyl ether.

[0130] A desirable UV binder is urethane acrylate resin, more particularly at least one isocyanate group-containing adduct of (a) an acrylic or methacrylic hydroxyl ester having 5 to 20 carbons atoms and (b) a polyisocyanate having 4 to 44 carbon atoms and 2 to 4 isocyanate groups. As examples of suitable isocyanate compounds may be mentioned hexamethylene disocyanate, 2,2,4-trimethylhexane-1,6-disocyanate,
2,4,4-trimethylhexane-1,6-diisocyanate, and cyclohexyl-1,4-diisocyanate, or the adduct of hexamethylene diisocyanate. Suitable photoinitiators include for example: aromatic carbonyl compounds such as benzyl, benzyl dimethyl ketal, acetophenone, substituted acetophenones, thiocyanate chloroform and preferably benzophenone. Optionally, use may be made of compounds such as aromatic azo compounds and compounds such as benzoin and ethers thereof, such as the methyl ether, the ethyl ether, the propyl ether and the 1-butyl ether. Mixtures of photoinitiators may also be used.

The photoinitiator is usually present in an amount of 0.05 to 10% by weight, based on the UV-curable binder. Some free radical polymerizations are inhibited by oxygen and may require provision of an inert atmosphere. Microencapsulation of components can help to restrict oxygen contact.

Preferably the binder in a UV reactive system is a reactive oligomeric prepolymer which polymerizes when subjected to UV radiation in the presence of a suitable initiator. An optional component of the binder can be commonly employed diluents which modify the cure rate and, for example, the viscosity of the uncured composition. The binder must be capable of adhering to the substrate on curing, but it should of course also wet or adhere to the substrate before curing.

The following is an illustrative example of a UV-curable binder. CN monomers are products of Sartomer (Exton, Pa.); CN550 (amine modified polyether acrylate oligomer) 53.2% by weight; CN501 (amine modified polyether acrylate oligomer) 22.8%; CN976 (urethane diacrylate) 20%; CN835 (benzophenone) 2%; and Irgacure 184 (photoinitiator) 2% (Ciba Specialty Chemicals). Viscosity at 25°C is about 2000 mPa.

The components of the second-part curative preferably are water soluble or water dispersible and are preferably external to the capsules. The components that are hydrophobic or oil soluble are preferably internal to the capsules. Most preferably the activator is selected to be hydrophobic and is separately encapsulated in a second population of microcapsules, separate and distinct from the first population of microcapsules encapsulating the monomer and first curative comprising initiator.

The second-part curative comprises a catalyst and activator. The second-part curative is external to the first population of polymeric microcapsules, on the outside capsule wall, or in the binder. In one embodiment, the monomer is a difunctional methacrylate, and the monomer can include in addition a monofunctional methacrylate, such as fururyl methacrylate. The difunctional methacrylate is preferably butylene glycol dimethacrylate, or hexane diol dimethacrylate.

Looking now at the drawings, FIG. 1 depicts an embodiment according to the invention. Monomer, and initiator which is the first-part curative, form the core of microcapsules 1, referred to herein as the first population of microcapsules. Catalyst 2A, a metallic salt or organic acid or metal ion, is shown outside of microcapsules 1. Sizes are exaggerated.

Activator 2B such as a tertiary amine, imide or amide can be separately encapsulated to form a second population of microcapsules. The microcapsule 5 for activator 2B in FIG. 1 is depicted using dotted lines since the encapsulation is optional. Other optional configurations for activator 2B include the arrangement of FIG. 4 wherein activator 2B is shown dispersed in a binder material 4 or carrier. The binder materials 4, 4', and 4" can be the same or different binders. The binder can constitute a matrix material or foam that temporarily isolates activator 2B from catalyst 2A.

An alternative arrangement with larger partial separation of catalyst 2A from activator 2B is depicted in FIG. 5. The binder materials 4, 4' and 4" can each be the same or different binders.

FIG. 2 illustrates the curable composition of the invention as a coating onto substrate 3 which can be any relatively rigid material such as glass, hardwood, fiberboard, plywood, oriented strandboard (OSB), chipboard, fiberglass, polymeric, natural or synthetic, composites such as fibers dispersed in various matrices such as resins, metals, or ceramics. The substrate should be selected to be receptive to the adhesive composition and should be tested for forming strong bonding with the adhesive composition. Medium-density fiberboard (MDF) and high-density fiberboard are suitable examples of fiberboard.

Dimensions are exaggerated in the drawings. The quantity of the binder is exaggerated and can be optionally limited to that quantity necessary to adhere the components of the adhesive system. It is therefore not always necessary to envelope the catalyst or activator, especially if these constituents are separately encapsulated.

FIG. 3 is an alternative embodiment wherein microcapsules 1 containing monomer and the first-part curative are dispersed in binder material 4 overcoated over lower binder material layer 4. The binder materials can be the same or different. Microcapsules 1 containing monomer and the first-part curative form a first population of microcapsules. A second population of microcapsules 5 is (shown smaller in size) and ellipsoid in shape for purposes of illustration. Size selection is optional and can be selected to be larger than the first population of microcapsules). The second population of microcapsules contain activator 2B within the core.

In FIG. 3, as a further alternative, the capsules 1, activator 2B, catalysts 2A can optionally be uniformly or chaotically dispersed in a single binder material 4 forming a single layer adhesive coating. The single layer adhesive coating is often preferable and most economic.

In FIG. 4 microcapsules 1 contain monomer and the first-part curative. The second-part curative of catalyst 2A and activator 2B is illustrated as dispersed in separate layers of binder material 4 and 4'. Binder materials 4, 4' and 4" can be the same or different in each layer. Microcapsules 1 are shown in the top binder layer 4'. Alternatively, microcapsules 1 can be dispersed throughout any of the binder material layers.

In FIG. 4 activator 2B is a lower layer and catalyst 2A forms a middle layer or is dispersed in a binder 4.

In FIG. 5 the second-part curative is disposed on opposite sides of the binder layer with microcapsules containing monomer and the first-part curative. Catalyst 2A is depicted below capsules 1, and activator 2B is illustrated applied as an overcoat on the opposite side of capsules 1 in binder 4". Optionally binder 4" can be omitted if adherence via binders 4' and 4 is sufficient to hold capsules 1, activator 2B and catalyst 2A in place.
FIG. 6 illustrates alternative embodiments A and B where the components of the adhesive system are coated onto separate surfaces 6 and 7. Surfaces 6 and 7 can take the form of a variety of mating or interlocking configurations such as the thread surfaces of a bolt and nut, mortise and tenon, dovetail, interlocking tongue and groove, snap-lock parts, male and female couplers, and various other configurations bringing at least two surfaces into proximate contact. Surfaces 6 and 7 can include a tab and corresponding recess, dent, friction fit or other mechanical interlock to facilitate holding the surfaces in place until the adhesive cures or sets. The adhesive system of the invention provides a dry-to-the-touch adhesive that can facilitate more permanent joining and assembly.

In FIG. 6, version A capsules 1 with first-part curative are shown applied to at least one face of surface 7. Catalyst 2A is also shown applied along with the first population of capsules 1.

A second population of capsules 5 encapsulating activator 2B is applied to at least one face of surface 6.

In FIG. 6, an alternative embodiment is also illustrated as version B wherein the catalyst 2A is applied to a face of surface 6 with the second population of capsules 5 which encapsulate activator 2B. Sufficient binder (not shown) should be utilized to adhere capsules 1 and 5 and catalyst 2A to hold them in position until the capsules are ruptured. This allows the free flowing liquid contents of the capsules to come into reactive contact such that the first-part curative and second-part curative can react with the monomer forming the structural adhesive.

As a yet further alternative embodiment, capsules 1 and 5 can be applied with binder to one or the same surface, and a catalyst 2A can be applied to a mating surface. All such variations are within the scope of the invention.

The examples herein are considered to illustrate the invention and should not be considered as limiting. In the examples all parts or proportions are by weight and all measurements are in the metric system, unless otherwise indicated.

EXAMPLE 1
Preparation of Microcapsules Containing 5% Initiator in Internal Phase

The composition of the capsules is as follows:

<table>
<thead>
<tr>
<th>Internal Phase (IP)</th>
<th>Hexanediol dimethacrylate,</th>
<th>156.9 g</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tetrahydrofurfuryl methacrylate,</td>
<td>17.4 g</td>
</tr>
<tr>
<td></td>
<td>Cumene hydroperoxide (CHP)</td>
<td>9.2 g</td>
</tr>
<tr>
<td>1st Water Phase:</td>
<td>Deionized water,</td>
<td>112 g</td>
</tr>
<tr>
<td></td>
<td>Acrylic acid butyl acrylate copolymer,</td>
<td>17.5 g</td>
</tr>
<tr>
<td></td>
<td>5% NaOH aqueous solution</td>
<td>14.1 g</td>
</tr>
<tr>
<td></td>
<td>methoxymethyl methacryl methacrylate,</td>
<td>2.9 g</td>
</tr>
<tr>
<td>2nd Water Phase:</td>
<td>Deionized water,</td>
<td>33.0 g</td>
</tr>
<tr>
<td></td>
<td>Polyacrylic acid,</td>
<td>6.1 g</td>
</tr>
<tr>
<td></td>
<td>Methoxymethyl methacryl methacrylate,</td>
<td>17.4 g</td>
</tr>
</tbody>
</table>

EXAMPLE 2
Preparation of Microcapsules Containing 1.5% Initiator in Internal Phase

The composition of and the procedures for preparing the microcapsules are the same as in Example 1 except for the following:

Internal Phase (IP) Hexanediol dimethacrylate, 162.6 g
Tetrahydrofurfuryl methacrylate, 18.1 g
Cumene hydroperoxide (CHP) 2.75 g

EXAMPLE 3
Preparation of Microcapsules Containing 2.5% Initiator in Internal Phase

The composition of and the procedures for preparing the microcapsules are the same as in Example 1 except for the following:

Internal Phase (IP) Hexanediol dimethacrylate, 161.0 g
Tetrahydrofurfuryl methacrylate, 17.9 g
Cumene hydroperoxide (CHP) 4.58 g

EXAMPLE 4
Preparation of Microcapsules Containing 5% Initiator in Internal Phase

The composition of and the procedures for preparing the microcapsules are the same as in Example 1 except for the following:

Internal Phase (IP) Hexanediol dimethacrylate, 162.6 g
Tetrahydrofurfuryl methacrylate, 18.1 g
Cumene hydroperoxide (CHP) 2.75 g

EXAMPLE 5
Preparation of Microcapsules Containing 5% Initiator in Internal Phase

The composition of and the procedures for preparing the microcapsules are the same as in Example 1 except for the following:

1st Water Phase: Deionized water, 112 g
Acrylic acid butyl acrylate copolymer, 9.1 g
5% NaOH aqueous solution 14.1 g
methoxymethyl methacryl methacrylate 2.9 g
2nd Water Phase: Deionized water, 33.0 g
Polyacrylic acid 6.1 g
methoxymethyl methacryl methacrylate 8.8 g
EXAMPLE 6
Preparation of Microcapsules Containing 1% Activator in Internal Phase

[0160] The composition of the capsules is as follows:

<table>
<thead>
<tr>
<th>Internal Phase (IP)</th>
<th>139.5 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexanediolmethacrylate</td>
<td></td>
</tr>
<tr>
<td>Tetrahydrofurfuryl methacrylate</td>
<td>34.8 g</td>
</tr>
<tr>
<td>Cumene hydroperoxide (CHP)</td>
<td>9.2 g</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1st Water Phase</th>
<th>112 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td></td>
</tr>
<tr>
<td>Acrylic acid butyl acrylate</td>
<td>17.8 g</td>
</tr>
<tr>
<td>copolymer</td>
<td></td>
</tr>
<tr>
<td>5% NaOH aqueous solution</td>
<td>13.6 g</td>
</tr>
<tr>
<td>methoxymethyl methylol melamine</td>
<td>2.9 g</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2nd Water Phase</th>
<th>32.0 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td></td>
</tr>
<tr>
<td>Polycrylic acid</td>
<td>6.1 g</td>
</tr>
<tr>
<td>Methoxymethyl methylol melamine</td>
<td>17.2 g</td>
</tr>
</tbody>
</table>

EXAMPLE 7
Preparation of Microcapsules Containing 5% Activator in Internal Phase

[0162] The composition of the capsules is as follows:

<table>
<thead>
<tr>
<th>Internal Phase (IP)</th>
<th>108 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexanediolmethacrylate</td>
<td></td>
</tr>
<tr>
<td>Tetrahydrofurfuryl methacrylate</td>
<td>12 g</td>
</tr>
<tr>
<td>3,5-diethyl-1,2-dihydro-1-phenyl-2-pyropyl pyridine</td>
<td>6.0 g (5%)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1st Water Phase</th>
<th>104 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td></td>
</tr>
<tr>
<td>Acrylic acid butyl acrylate</td>
<td>18 g</td>
</tr>
<tr>
<td>copolymer</td>
<td></td>
</tr>
<tr>
<td>5% NaOH aqueous solution</td>
<td>14 g</td>
</tr>
<tr>
<td>methoxymethyl methylol melamine</td>
<td>3.0 g</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2nd Water Phase</th>
<th>32.0 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td></td>
</tr>
<tr>
<td>Polycrylic acid</td>
<td>6.0 g</td>
</tr>
<tr>
<td>Methoxymethyl methylol melamine</td>
<td>17.7 g</td>
</tr>
</tbody>
</table>

EXAMPLE 8
Preparation of Microcapsules Containing Only Activator in Internal Phase

[0164] The composition of the capsules is as follows:

<table>
<thead>
<tr>
<th>Internal Phase (IP)</th>
<th>183 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,5-diethyl-1,2-dihydro-1-phenyl-2-pyropyl pyridine</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>1st Water Phase</th>
<th>112 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td></td>
</tr>
<tr>
<td>Acrylic acid butyl acrylate</td>
<td>17.8 g</td>
</tr>
<tr>
<td>copolymer</td>
<td></td>
</tr>
<tr>
<td>5% NaOH aqueous solution</td>
<td>13.6 g</td>
</tr>
<tr>
<td>methoxymethyl methylol melamine</td>
<td>2.9 g</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2nd Water Phase</th>
<th>32.0 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td></td>
</tr>
<tr>
<td>Polycrylic acid</td>
<td>6.1 g</td>
</tr>
<tr>
<td>Methoxymethyl methylol melamine</td>
<td>17.2 g</td>
</tr>
</tbody>
</table>

EXAMPLE 9
Preparation of Microcapsules Containing 5% Activator in Internal Phase

[0166] The composition of and the procedures for preparing the microcapsules are the same as in Example 7 except for the following:

<table>
<thead>
<tr>
<th>1st Water Phase</th>
<th>112 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td></td>
</tr>
<tr>
<td>Acrylic acid butyl acrylate</td>
<td>9.1 g</td>
</tr>
<tr>
<td>copolymer</td>
<td></td>
</tr>
<tr>
<td>5% NaOH aqueous solution</td>
<td>14.1 g</td>
</tr>
<tr>
<td>methoxymethyl methylol melamine</td>
<td>2.9 g</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2nd Water Phase</th>
<th>33.0 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water</td>
<td></td>
</tr>
<tr>
<td>Polycrylic acid</td>
<td>6.1 g</td>
</tr>
<tr>
<td>Methoxymethyl methylol melamine</td>
<td>8.8 g</td>
</tr>
</tbody>
</table>
EXAMPLE 10

Preparation of Microcapsules Containing Only Activator in Internal Phase

[0167]

Internal Phase: PDHP (3,5-diethyl-1,2-dihydro-1-phenyl-2-pyropyl pyridine) 290 g

Water Phase I
- Water 230.4 g
- Acrylic acid butyl acrylate copolymer 3.0 g
- 5% NaOH 22.1 g
- Methoxymethyl methylen melamine 4.8 g

Water Phase II
- Water 126 g
- Polycrylic acid 10.1 g
- Methoxymethyl methylen melamine 29.2 g

[0168] A general procedure of capsule manufacture is described. 290 grams of 3,5-diethyl-1,2-dihydro-1-phenyl-2-pyropyl pyridine (PDHP) is selected as an internal phase. The second water phase is added along with 3.8 grams Na₂SO₄ and the mixture heated for 8 hours at 65°C. Capsules of approximately 26 μm size are obtained.

EXAMPLE 11

Adhesive Coating Formulation

[0172] Capsules containing initiator and capsules containing activator were mixed with catalyst and binders, and were coated on cellulosic substrate made of high density fiber boards. Alternatively catalyst may be pre-applied on the substrate, mixed in the liquid coating formulation, or applied in both. The binder used was a vinyl acetate-ethylene copolymer latex. After the coating was dried, two pieces of substrate with the coating applied using a snap-fit tongue and groove assembly were mated together, and the compression fit exerted sufficient shear force to break the capsules in the coating, resulting in reactive contact among initiator, activator, monomers and catalyst. Table 4 shows the bonding strength tested with an EJA Materials Tester (Thwin-Albert Company).

Table 4

<table>
<thead>
<tr>
<th>Test #</th>
<th>Initiator Capsules</th>
<th>Activator Capsules</th>
<th>Capsule Ratio of Initiator to Activator</th>
<th>Binder (%)</th>
<th>Copper pre-coat (ppm)</th>
<th>Strength (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Example 1</td>
<td>Example 7</td>
<td>1/1</td>
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<td>Yes</td>
<td>740</td>
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<tr>
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<td>Example 7</td>
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<td>Yes</td>
<td>1480</td>
</tr>
<tr>
<td>3</td>
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<td>1/1</td>
<td>5</td>
<td>Yes</td>
<td>740</td>
</tr>
<tr>
<td>4</td>
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<td>5</td>
<td>Yes</td>
<td>1480</td>
</tr>
<tr>
<td>5</td>
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<td>1/1</td>
<td>5</td>
<td>No</td>
<td>4400</td>
</tr>
<tr>
<td>6</td>
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<td>Example 9</td>
<td>1/1</td>
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<td>1480</td>
</tr>
<tr>
<td>7</td>
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<td>5</td>
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<td>1480</td>
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<td>8</td>
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<td>1/2</td>
<td>0</td>
<td>No</td>
<td>1480</td>
</tr>
<tr>
<td>9</td>
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<td>1480</td>
</tr>
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<td>10</td>
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<td>1/2</td>
<td>5</td>
<td>Yes</td>
<td>1480</td>
</tr>
<tr>
<td>11</td>
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<td>Example 8</td>
<td>1/99</td>
<td>5</td>
<td>Yes</td>
<td>1480</td>
</tr>
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<td>12</td>
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<td>1480</td>
</tr>
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<td>1480</td>
</tr>
<tr>
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<td>Example 8</td>
<td>1/99</td>
<td>5</td>
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</tr>
<tr>
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<td>Example 8</td>
<td>1/99</td>
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</tr>
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<td>16</td>
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<td>Example 10</td>
<td>1/99</td>
<td>5</td>
<td>No</td>
<td>4400</td>
</tr>
</tbody>
</table>

EXAMPLE 12

Initiator and Activator Capsules Coated on Separate Substrates

[0174] Capsules containing initiator and capsules containing activator may be separately formulated with other coating components, such as catalyst and binders. In the following table, these were coated on separate substrates to be bonded. Table 5 shows bonding strength tested with an EJA Materials Tester (Thwin-Albert Company).

[0169] A first water phase is prepared of 230.4 grams water, 3 grams of acrylic acid butyl acrylate copolymer, and 4.8 grams methoxymethyl methylen melamine. pH is adjusted to 5.68 with 5% NaOH.

[0170] A second water phase is prepared of 126 grams of water, 10.1 grams polycrylic acid, and 29.5 grams methoxymethyl methylen melamine.

[0171] Water phase 1 is maintained at 65°C. with stirring (500 rpm). The internal phase is added and stirring increased to blend at high speed to achieve an emulsion size of 27.1 μm.
### TABLE 5
Bonding strength for capsules coated on separate substrates

<table>
<thead>
<tr>
<th>Test #</th>
<th>Capsule 1</th>
<th>Capsule 2</th>
<th>Ratio of Copper to Initiator</th>
<th>Initiator to Activator</th>
<th>Binder (%)</th>
<th>Copper in slurry (ppm)</th>
<th>Strength (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Example 1</td>
<td>Example 7</td>
<td>1/1</td>
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<td>Yes</td>
<td>1480</td>
<td>156</td>
</tr>
<tr>
<td>2</td>
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<td>Example 7</td>
<td>1/1</td>
<td>5</td>
<td>Yes</td>
<td>1480</td>
<td>442</td>
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<td>3</td>
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<td>Example 6</td>
<td>1/2</td>
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<td>1480</td>
<td>772</td>
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<tr>
<td>4</td>
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<td>Example 6</td>
<td>1/2</td>
<td>5</td>
<td>Yes</td>
<td>1480</td>
<td>961</td>
</tr>
<tr>
<td>5</td>
<td>Example 1</td>
<td>Example 8</td>
<td>1/99</td>
<td>5</td>
<td>Yes</td>
<td>1480</td>
<td>896</td>
</tr>
<tr>
<td>6</td>
<td>Example 5</td>
<td>Example 10</td>
<td>1/99</td>
<td>5</td>
<td>No</td>
<td>4400</td>
<td>966</td>
</tr>
</tbody>
</table>

### EXAMPLE 13
Different Binders

Many different kinds of binder materials can be used in the coating formulation. They should be able to hold capsules and other components of the coating in place, and has no adverse effect on bonding strength. The following binders were tested:

- **A**—Vinyl acetate-ethylene copolymer
- **B**—Acrylic latex
- **C**—Carboxylated vinyl acetate resin
- **D**—Polyvinyl acetate

**TABLE 6**
Bonding strength with different binders

<table>
<thead>
<tr>
<th>Binders</th>
<th>Capsule 1</th>
<th>Capsule 2</th>
<th>Ratio of Initiator to Activator</th>
<th>Binder (%)</th>
<th>Copper in slurry (ppm)</th>
<th>Strength (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Example 1</td>
<td>Example 7</td>
<td>1/1</td>
<td>5</td>
<td>Yes</td>
<td>1480</td>
</tr>
<tr>
<td>B</td>
<td>Example 1</td>
<td>Example 7</td>
<td>1/1</td>
<td>5</td>
<td>Yes</td>
<td>1480</td>
</tr>
<tr>
<td>C</td>
<td>Example 1</td>
<td>Example 7</td>
<td>1/1</td>
<td>5</td>
<td>Yes</td>
<td>1480</td>
</tr>
<tr>
<td>D</td>
<td>Example 1</td>
<td>Example 7</td>
<td>1/1</td>
<td>5</td>
<td>Yes</td>
<td>1480</td>
</tr>
</tbody>
</table>

### EXAMPLE 14
Viscosity of monomer blends as the internal phase of capsules. M corresponds to THFA/HDDMA 50/50 ratio

**Viscosity (cps, 25°C)**

- Melamine acrylate oligomer (Doresco UV75, C1, 1500 cps/M 50/50 ratio) Approx. 15
- Bisphenol A base epoxide acrylate (CN120, 2150 cps @ 65°C) Approx. 25
- M 40/60 ratio Approx. 53
- Urethane dimethacrylate (CN 1963, 1746 cps @ 65°C)/M 50/50 ratio Approx. 25
- Polybutadiene (Ricon 130, 750 cps)/M 50/50 ratio Approx. 25

The above blends can contain up to 5% by weight of DPC activator or CHP initiator. HDDMA is hexanediol dimethacrylate. THFA is tetrahydrofururyl methacrylate.

**We claim:**

1. A surface element, having at least one of a tongue and a groove, comprising:
   - a dry glue disposed on at least one surface of the flooring element, wherein, when activated, said dry glue exhibits a creep strength of between 1 and 50 kN/m, when measured with a gap less than 0.1 mm and a pull rate of 0.02 mm/min.
   - The surface element of claim 1, wherein the dry glue is a pregel.

2. The surface element of claim 1, wherein, when activated, said dry glue exhibits a creep strength of between 7 and 20 kN/m, when measured with a gap less than 0.1 mm and a pull rate of 0.02 mm/min.

3. The surface element of any of the preceding claims, wherein said dry glue, when activated, further exhibits at least one property selected from the group consisting of:
   - a tensile strength of 7-20 kN/m when measured with a gap less than 0.1 mm and a pull rate of 2 mm/min;
   - storage stability of at least one year;
   - low initial tack value; and
   - set time of at least 45 minutes.

**CN polymers and Ricon™ are trademarks of Sartomer (Exton, Pa.). Doresco™ is a trademark of Lubrizol (Wickliffe, Ohio). CHP is cumene hydroperoxide; DPC is diphenyl carbazone; CN120 is bisphenol epoxy acrylate.**
5. The surface element of any of the preceding claims, wherein said dry glue when activated, further exhibits each of:
   a tensile strength of 7-20 kN/m when measured with a gap less than 0.1 mm and a pull rate of 2 mm/min;
   a storage stability of at least one year;
   a low initial tack value; and
   a set time of at least 45 minutes.
6. The surface element of any of the preceding claims, wherein said dry glue is positioned on said at least one of a tongue and a groove.
7. The surface element of any of the preceding claims, wherein said dry glue comprises at least one component selected from the group consisting of:
   a monomer;
   an initiator;
   an activator; and
   a catalyst.
8. The surface element of claim 7, wherein said at least one of said at least one component is encapsulated.
9. The surface element of claim 7 or 8, wherein said at least one component is said monomer.
10. The surface element of any of claims 6-9, wherein said dry glue further comprises a second component selected from the group consisting of:
    a monomer;
    an initiator;
    an activator; and
    a catalyst,
wherein said second component is not encapsulated with said first component.
11. The surface element of claim 10, wherein said second component is encapsulated.
12. The surface element of any of claims 1-11, wherein the surface element is a flooring element, and comprises:
    a core material;
    a decorative surface on the core material, and
    a wear layer disposed on the decorative surface.
13. A surface system comprising:
    a plurality of surface elements according to any of the preceding claims, wherein at least one of said plurality of flooring elements comprises a tongue and at least one of said plurality of flooring elements comprises a groove.
14. The surface system of claim 13, wherein said dry glue comprises at least two components selected from the group consisting of:
    a monomer;
    an initiator;
    an activator; and
    a catalyst,
wherein at least one component is present on said tongue and at least one component is present in said groove.
15. The surface system of claim 14, wherein said at least one component on said tongue is different than said at least one component in said groove.
16. The surface system of claim 14 or 15, wherein at least one of said components is encapsulated.
17. The surface system of claim 16, wherein said encapsulated component is said monomer.
18. The surface system of claim 15, wherein said encapsulated monomer is present on one of said tongue and said groove, and at least one selected from the group consisting of an initiator; an activator; and a catalyst is present on the other of said tongue and said groove.
19. The surface system of any of claims 11-18, wherein at least one of said tongue and said groove comprise locking elements.
20. A method of forming a substantially planar surface comprising:
    providing a first surface element of any of claims 1-12;
    activating said dry glue; and
    joining said surface element with a second element.
21. The method of claim 20, wherein the dry glue further exhibits at least one property selected from the group consisting of:
    tensile strength of 7-20 kN/m when measured with a gap less than 0.1 mm and a pull rate of 2 mm/min;
    storage stability of at least one year;
    low initial tack value; and
    set time of at least 45 minutes.
22. The method of claim 21, wherein said second surface element is a surface element of any of the preceding claims.
23. The method of claim 20 or 21, wherein said first surface element comprises a tongue and said second surface element comprises a groove, wherein at least first component of said preglue is present on at least one of said tongue and said groove.
24. The method of any of claims 20-23, wherein said activating comprises mating said tongue and said groove.
25. A method of forming a substantially planar flooring system comprising:
    providing a first flooring element having a preglue on at least one surface of said first flooring element thereon,
    wherein the preglue exhibits a creep strength of between 1 and 50 kN/m, when measured with a gap less than 0.1 mm and a pull rate of 0.02 mm/min;
    activating the preglue; and
    joining the first flooring element with a second flooring element.
26. The method of claim 25, wherein the preglue exhibits a creep strength of between 7 and 20 kN/m, when measured with a gap less than 0.1 mm and a pull rate of 0.02 mm/min.
27. The method of claim 25 or 26, wherein the preglue further exhibits at least one property selected from the group consisting of:
    tensile strength of 7-20 kN/m when measured with a gap less than 0.1 mm and a pull rate of 2 mm/min;
    storage stability of at least one year;
    low initial tack value; and
    set time of at least 45 minutes.
28. The method of any of claims 25-27, wherein said activating comprises rupturing microballoons containing at least one component of the preglue.
29. The method of any of claims 25-28, wherein said activating comprises rupturing a tongue-and-groove system of the first and second flooring elements.
30. The method of any of claims 25-29, wherein said activating comprises contacting a first component of the preglue, the first component positioned on the first flooring element, with a second component of the preglue, the second component positioned on the second flooring element.

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