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(54) Title: MALONATES AND DERIVATIVES FOR IN-SITU FILMS

(57) Abstract: The present teachings contemplate a method comprising coating an polymeric material with a composition including a dicarbonyl compound and having a viscosity of from about 50 cps to about 500 cps, wherein the coating initiates either: (i) spontaneous polymerization (e.g., in less than about one minute) at room temperature of the composition without the addition of an initiator; or (ii) polymerization at room temperature at a selected later time with or without the addition of an initiator; and wherein the composition adheres or facilitates adhesion of the polymeric material to a substrate.

MALONATES AND DERIVATIVES FOR IN-SITU FILMS

Technical Field

[0001] The present invention relates generally to malonate coatings, films or similar treatments that allow for easily controlled polymerization.

Background

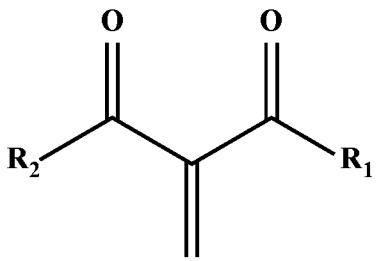
[0002] In the transportation and construction industries, among others, polymeric adhesives, sealants and foams are frequently used to provide structural support, sealing, and sound attenuation. Coatings, handling films, or the like (referred to herein generally as coatings) are frequently utilized in conjunction with such materials. However, many such coatings or even the adhesives, sealants or foams themselves present significant challenges in adhering to certain substrates, especially substrates that may be coated with contaminates such as oil. Furthermore, many existing coatings require the addition of an initiating substance or environment in order to polymerize and adhere during application to a substrate

[0003] United States Patent Nos. 8,609,885; 8,884,051; and 9,181,365 and U.S. Publication Nos. 2014/0329980 and 2015/0056879 may be relevant to the present teachings, and are all incorporated by reference for all purposes.

[0004] Notwithstanding the above teachings, there has remained a need for coatings that are capable of polymerization at room temperature upon contact with certain substrates without need for any initiator. There is a further need for coatings that are capable of adhering to substrates that typically present challenges in adhesion, especially contaminated substrates.

Summary of the Invention

[0005] One or more of the above needs are met by the present teachings which contemplate a method comprising coating a material with a composition including a dicarbonyl compound represented by the formula

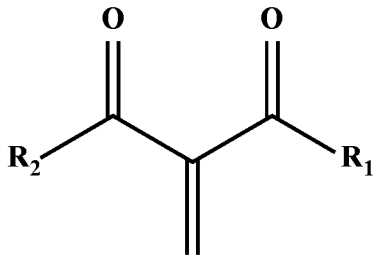


the composition having a viscosity of from about 50 cps to about 500 cps, wherein the coating process initiates either: (i) spontaneous polymerization (e.g., in less than about one minute) at room temperature of the composition without the addition of an initiator; or (ii) polymerization at room temperature at a selected later time with or without the addition of an initiator; and wherein the composition assists in adhering the coated material to a substrate (e.g., by permitting penetration of the material through the coating to the substrate).

[0006] The material which receives the coating may be a polymeric material. The material may be an expandable material. The substrate to which the coated material is adhered may be a metallic material. The substrate may be a contaminated substrate (e.g., coated in oil or the like). The substrate may be a polycarbonate material. One or more of the substrate and material may be nucleophilic. The substrate and/or material may have a pH of greater than 7. The coating step may comprise applying the composition to the material as a film. The coating step may include spray coating, roll coating, brushing, dipping or any combination thereof. The composition may form a handling film. Polymerization of the composition may occur at least 5 minutes, at least 15 minutes or even at least 30 minutes after coating. Polymerization of the composition may occur less than 1 hour, less than 30 minutes, less than 15 minutes, or even less than 5 minutes after coating. The substrate may be a sheet molding compound (SMC) material. The composition may be stored in a container comprising one or more materials having a neutral pH (e.g., a pH of less than 7). The composition may be formed as a paste. The composition may include a colorant. One or more of the material and/or substrate may be formed with a bisphenol A precursor. The method may include welding the material after coating. The coated material may be a tape. The tape may include a first surface containing a pressure sensitive adhesive. The tape may include a surface that is a heat activated adhesive. The coated material may form a laminate when applied to the substrate. The composition may be formed for locating into a glue gun application device. The composition may be stored in a polyethylene container. The substrate may be concrete. The substrate may be coated with an oil-based substance. The oil-based substance may be 61 MAL HCL 1. The coating may form a tack-free surface on the material. The method may include heating the coated material on the substrate to cause adhesion of the composition and/or material to the substrate. The material may be a tacky material. The material may be a tack-free material. The material may be an epoxy-containing material. The material may include an ethylene copolymer. The composition may include one or more of a diethyl (e.g., diethyl methylmalonate), dimethyl, hexyl methyl, ethyl ethoxy ethyl, ethyl cyclohexyl, 2-phenylpropyl ethyl, dicyclohexyl, and fenchyl methyl.

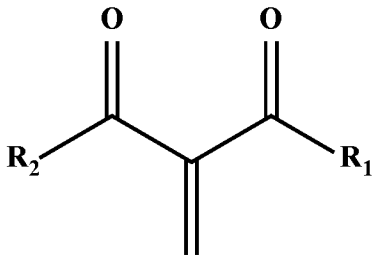
[0007] The material may be a structural adhesive. The composition may increase dimensional stability of the adhesive. A reinforcing layer may be added to the material and composition so that the reinforcing layer is: (i) located on the surface of the material; (ii) located within (e.g., substantially surrounded by) the material; (iii) formed as a bead of extruded material; or (iv) any combination thereof. A reinforcing layer may be added to the material and composition and the reinforcing layer may comprise a scrim, a yarn, a fiber, a bead of solid epoxy-containing material, a weave, fibers (e.g., glass, carbon, Kevlar or the like), a mesh, or any combination thereof. One or more of the material or composition may include a thermoplastic epoxy component. A reinforcing layer may be added to the material and composition and the reinforcing layer may be a recyclable material. The material may be selected from a sealant, and adhesive, a patch, a tape, or any combination thereof. The composition and material may be reprocessed (e.g., recyclable) without property degradation of the material. The material may penetrate the composition and adhere to the underlying substrate. The coating may improve the handling of the material. The coating may improve the adhesion of the underlying material. The coating may improve the weldability of the material. The weldability may be improved by the composition modifying one or more physical characteristics of the material to which it is applied. The weldability may be improved by modifying the one or more of the rheology and/or surface characteristics of the material by use of the coating.

[0008] The teachings herein further provide for a structure comprising a polymeric material, a composition including a dicarbonyl compound represented by the formula



coated located onto the polymeric material and a substrate having a pH of greater than 7 located in contact with the composition.

[0009] The teachings herein also provide for a method comprising coating n polymeric material with a composition including a dicarbonyl compound represented by the formula



and having a viscosity of from about 50 cps to about 500 cps, wherein the coating polymerizes upon the addition of an initiator and wherein the composition adheres the polymeric material to a substrate and/or the polymeric material penetrates the composition to adhere to the substrate.

[00010] The present teachings further contemplate a device comprising an expandable material, an open mesh weave located in planar contact with the expandable material and along the entirety of the expandable material, and a malonate handling film applied to at least a portion of open mesh/expandable material assembly. The expandable material may be tacky prior to expansion allowing the expandable material to adhere to the open mesh weave. It also may allow, prior to expansion, adhesion to a surface for reinforcing the surface, at least in desired areas, but with allowing efficiently and effectively handling from the manufacturing line of the device, to the installation in the vehicle.

[00011] The device may be configured to conform to the shape of the surface. The device may be flexible (e.g., capable of easily bending without breaking) prior to expansion of the expandable material. The device may bend under its own weight when held at its end. The volumetric activation of the activatable material may be at least about 100% and less than about 300%. The expandable material may include a structural adhesive material. The expandable material may include a sealant material.

[00012] The present teachings further contemplate a method for structurally reinforcing a vehicle body stamping comprising forming a tacky expandable structural adhesive material and locating an open mesh material onto the expandable material. The method may further include applying a handling coating to all or part of the open mesh/expandable material assembly. The coating may comprise a malonate composition which may be a malonate film. The method may further include contacting the open mesh and expandable material with a vehicle body stamping surface and activating the expandable material to expand by application of heat. The open mesh and expandable material may remain in contact with the stamping surface by means of the tacky nature of the expandable material in a portion not covered by the handling coating or via another attachment method, prior to activating the expandable material.

[00013] The method may be free of any separate fastening step for connecting the reinforcement member to the body stamping. The method may include a separate fastening step for connecting the reinforcement member to the body stamping. The method may include flexing the expandable material and mesh to conform to the shape of the body stamping prior to activating the expandable material. The method may include cutting the expandable material to a desired shape prior to locating the mesh onto the expandable material. The method may include cutting the expandable material and mesh located thereon to a desired shape prior to contacting the mesh and expandable material with the vehicle body stamping surface. The step of forming the tacky expandable structural adhesive material may be free of any molding process. The step of locating the mesh onto the expandable material may be free of any separate fastening step for connecting the mesh to the expandable material. The step of activating the expandable material includes volumetric expansion of at least about 100% and less than about 300%. The method may include flexing the expandable material and mesh so that a first portion of the mesh and expandable material is arranged at an angle of 90° or less from a second portion of the mesh and expandable material. The method may include flexing the expandable material and mesh so that a surface of the vehicle body stamping is contacted by the mesh and expandable material that would not be contacted by the mesh and expandable material if the mesh and expandable material were substantially rigid. The mesh may be located onto the expandable material so that the expandable material substantially covers the mesh and is free of any voids on the mesh that are not covered with the expandable material prior to activation. The open mesh and expandable material may no longer be flexible after activation of the expandable material. The open mesh and expandable material may continue to be flexible after activation of the expandable material.

Detailed Description

[00014] The explanations and illustrations presented herein are intended to acquaint others skilled in the art with the invention, its principles, and its practical application. Those skilled in the art may adapt and apply the invention in its numerous forms, as may be best suited to the requirements of a particular use. Accordingly, the specific embodiments of the present invention as set forth are not intended as being exhaustive or limiting of the teachings. The scope of the teachings should, therefore, be determined not with reference to the above description, but should instead be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles and references, including patent applications and publications, are incorporated by reference for all

purposes. Other combinations are also possible as will be gleaned from the following claims, which are also hereby incorporated by reference into this written description.

[00015] This application is related to and claims the benefit of the priority date of U.S. Provisional Application Serial Nos. 62/325,818, filed on April 21, 2016; 62/396,435, filed on September 19, 2016; and 62/395,012, filed on September 15, 2016. The entirety of these applications are hereby incorporated by reference for all purposes.

[00016] The present teachings contemplate the use of a malonate-based composition (e.g., a monomeric composition) for coating (e.g., applying as film to) a secondary material (which may be a polymeric material). Any reference herein to the material to which the coating is applied may be referring to the material in its unactivated (e.g. uncured or green) state or in its activated (e.g., cured) state. The composition may preferably comprise a diethyl malonate (DEM). The composition may comprise a dimethyl malonate (DMM). The composition may preferably comprise a diethyl methylmalonate (DEMM). The composition may include one or more additional components which may be selected from adhesion promoters and initiators. The composition may include a cyanoacrylate (e.g., methyl 2-cyanoacrylate, ethyl-2-cyanoacrylate, n-butylcyanoacrylate and 2-octylcyanoacrylate). The composition may include one or more of a diethyl, dimethyl, hexyl methyl, ethyl ethoxy ethyl, ethyl cyclohexyl, 2-phenylpropyl ethyl, dicyclohexyl, and fenchyl methyl.

[00017] The malonate composition may be a one part material that polymerizes either immediately or at some later designated time at room temperature (e.g., at a temperature of from about 20º C to about 25º C). It is also possible that some heat may be utilized for polymerization. It is quite possible that the malonate composition polymerizes at room temperature without the addition of any initiator or stimulus. However, it is also possible that an initiator or stimulus may be utilized to cause polymerization of the composition. Suitable stimuli includes but are not limited to ultra-violet light. The composition may be such that the time of polymerization can be modified so that it is “on demand”. In other words, the composition can be applied as a coating (e.g. as a film) to a secondary material to provide sufficient open time for application of the coating with no polymerization such that the composition does not polymerize until contact with a substrate of choice. Thus, open time for the application process can extend a number of minutes or even an hour without fear of early polymerization. It is possible that only contact with certain substrates initiates polymerization of the composition.

[00018] The teachings herein are also directed to a method whereby a material that has one or more characteristics that make it difficult to handle (e.g., that the material is tacky, that it

is subject to sag, that the viscosity is lower than desired, that the surface energy is lower than desired) is coated with a composition to assist in ameliorating one or more of these characteristics. The surface of the material that receives the coating may then be located onto a substrate. The substrate may be a material that is typically difficult to adhere to, whether by the physical characteristics of the substrate itself, or the presence of a treatment (e.g., oil) that presents challenges for adhering. The properties of the substrate may be selected such that upon contact with the material the composition polymerizes. However, it is also possible that the composition polymerizes upon contact with the substrate. It is possible that the composition remains as a layer between the material and the substrate. It is possible that the composition improves adhesion between the material and the substrate. It is possible that the material permeates the composition coating to adhere directly to the substrate. It is possible that only the composition adheres to the substrate. The material may be an activatable material such that upon coating the material with the composition, the material is in its unactivated or “green” state. Thus, despite the fact that the material adheres sufficiently upon activation, the composition may assist in adhering the material to the substrate prior to activation.

[00019] At some later time, after applying the coated material to a substrate, the material may be activated by the addition of a stimulus. The stimulus may be a physical stimulus or chemical stimulus. The material may be activated by the addition of heat. Upon activation, the material may expand and/or otherwise cure forming a more rigid material that is generally dry to the touch, but may possibly remain tacky.

[00020] The coating may provide one or more of the following benefits. The coating may form a tack-free surface on an otherwise tacky material. The coating may adhere the secondary material to a substrate. The coating may be such that the secondary material may permeate the coating so that the secondary material adheres to the substrate. The coating may undergo polymerization at room temperature with no additional initiator or stimulus. The coating may allow for de-bonding of the secondary material from a substrate. The coating may provide sufficient adhesion of the secondary material to substrates which are generally difficult to adhere to. The coating may provide sufficient adhesion to contaminated surfaces such as those coated in oil-based substances. The coating may improve the weldability of a material to which the coating is applied. The coating may improve tack and/or adhesion. The coating may allow for the addition of a color or other appearance attribute. The coating may improve the energy absorption of a material to which the coating is applied. The coating may improve the reflectivity of a surface to which it is applied. The coating may improve the tactile safety of a surface to

which the coating is applied. The coating may assist in minimizing abrasion of the material. The coating may act to absorb one or more contaminants present on one or more of the material, the substrate or both. The coating may be a formulation that facilitates simplified reprocessing. For example, the underlying material may be easily recycled or reprocessed with the coating still located thereon with minimal or no degradation to the material.

[00021] As mentioned, the composition may be applied to a secondary polymeric material. Immediate polymerization at room temperature may occur when the coated polymeric material is applied to the secondary material. Polymerization may occur only upon contact of the composition with a substrate (after application of the composition to the secondary material). It is also possible that that the composition may polymerize via electropolymerization, mechanically initiated polymerization, dual cure polymerization, thermally initiated polymerization, coordination polymerization, or nucleophilic polymerization. The composition may undergo solution or emulsion polymerization. It is also possible that the composition undergoes random copolymerization or block copolymerization. The composition may undergo anionic polymerization. The composition may undergo free radical polymerization.

[00022] When selecting the composition to utilize as a coating for a polymeric material, one or more of glass transition temperature (T_g), flexibility, reactivity, toughness, adhesion capability, rigidity, speed of reactivity or heat resistance may provide motivation for such selection. The coating may preferably be a malonate material. As a non-limiting example, a diethyl material may provide rapid reactivity. A dimethyl material may provide high reactivity. A hexyl methyl material may provide flexibility and toughness. An ethyl ethoxy ethyl material may provide improved adhesion and flexibility. An ethyl cyclohexyl material may provide rigidity, stiffness and rapid reactivity. A 2-phenylpropyl ethyl material may provide stiffness and improved adhesion. A dicyclohexyl material may provide a high T_g, stiffness and heat resistance. A fenchyl methyl material may provide high T_g, high rigidity, slow reactivity and heat resistance. Accordingly, depending on the intended use of the secondary polymeric material and the intended substrate upon which the polymeric material may be located, it is possible to select a coating which provides attributes which will benefit the intended use.

[00023] Polymeric materials coated with the compositions taught herein may have improved properties as compared to the polymeric materials with no coating. The coated polymeric materials may have improved mechanical properties such as increased tensile strength, improved modulus, improved hardness, increase impact strength, increased UV stability and improved crystallinity. The coated polymeric materials may have improved barrier

capabilities against oxygen, carbon dioxide, water and other substances. The coated polymeric materials may have improved rheology, ductility and elasticity. The coated polymeric materials may have improved thermal characteristics and higher heat distortion temperatures. The coated polymeric materials may have improved electrical properties, improved optical properties, and improved thermodynamic properties. The coating may modify the surface energy of the polymeric material and improve wetting and adhesion. The thermodynamic nature and surface energy characteristics of the coating compositions may account for the ability of the compositions to adhere to oily substrates.

[00024] It is possible that contact between the coating composition and certain substrates may cause polymerization of the coating compositions. Certain basic substrates (e.g., those having a pH of greater than 7) may cause polymerization (and thus possibly adhesion) of the coating composition, which may thus adhere the secondary polymeric material to the substrate. It is also possible that acidic substrates (e.g., those having a pH of less than 7) may not cause polymerization of the coating composition. However, the coating may be utilized in systems having materials and/or substrates with pH of lower than 7, but an initiator may be required for the coating to polymerize. It is also possible that the more basic a substrate (the higher the pH) the more quickly the coating composition will polymerize. Thus, acidic materials may be included in the system to slow polymerization if so desired. Nucleophilic substrates may also initiate polymerization of the coating composition. It is possible that increased nucleophilicity will initiate polymerization more quickly. Some examples of substrates which act to initiate polymerization of the coating compositions disclosed herein include polycarbonate, SMC, Kevlar, concrete or other basic substrates. Some examples of substrates where the coating compositions may not polymerize, thereby possibly requiring an initiator or stimulus, include polyethylene, polypropylene and Teflon.

[00025] The coating compositions may be utilized in the formation of tapes (which may be pressure sensitive), or any material requiring differential tack. The coating compositions may be utilized to form weldable materials. The adhesion capability of the coating compositions may be modified by raising the molecular weight of the coating composition. Adhesion may occur upon initiation but may also be delayed post-initiation.

[00026] The material to which the coating is applied may be at least partially tacky at room temperature (e.g., about 23° C.) and may also be tacky at temperatures between about 0° C. and about 80° C. Additionally, the material preferably exhibits reinforcement characteristics (e.g., imparts rigidity, stiffness, strength or a combination thereof to a member) upon cure when

located onto a substrate. It is also preferable for the material to be heat activated to expand or otherwise activate and wet surfaces which the material contacts. After expansion or activation, the material preferably cures, hardens and adheres to the surfaces that it contacts. For application purposes, it is often preferable that the material exhibit flexibility, particularly when the material is to be applied to a contoured surface of a vehicle body. Once applied, however, it is typically preferable for the material to be activatable to soften, expand (e.g., foam), cure, harden or a combination thereof. For example, and without limitation, a typical material will include a polymeric material, such as an epoxy resin or ethylene-based polymer which, when compounded with appropriate ingredients (typically a blowing and curing agent), expands and cures in a reliable and predicable manner upon the application of heat or the occurrence of a particular ambient condition. From a chemical standpoint for a thermally-activated material, the material may be initially processed as a flowable material before curing. Thereafter, the base material preferably cross-links upon curing, which makes the material substantially incapable of further flow.

[00027] The material may be an epoxy-based material which may be aliphatic, cycloaliphatic, aromatic or the like. The epoxy may be supplied as a solid (e.g., as pellets, chunks, pieces or the like) or a liquid. The epoxy may include an ethylene copolymer or terpolymer that may possess an alpha-olefin. As a copolymer or terpolymer, the polymer is composed of two or three different monomers, i.e., small molecules with high chemical reactivity that are capable of linking up with similar molecules. One exemplary epoxy resin may be a phenolic resin, which may be a novalac type or other type resin. Other preferred epoxy containing materials may include a bisphenol-A epichlorohydrin ether polymer, or a bisphenol-A epoxy resin which may be modified with butadiene or another polymeric additive. Examples of suitable epoxy-based materials, which may be used as in the base material are sold under the product designations L5020, L5010, L5224, L8000, L5001 and are commercially available from L&L Products, Romeo, Mich. According to preferred formulations, the base material can include up to about 50% by weight epoxy resins, more preferably, up to about 65% by weight epoxy resins, and even more preferably up to about 80% by weight epoxy resins.

[00028] A substantial portion of the materials in the material will typically have molecular weights that are low enough to maintain adhesive capability of the base material. For an elastomer-based or epoxy-based base material, it is preferable for at least about 5% by weight of the elastomer or epoxy materials to have a molecular weight less than about 1000 and more preferably at least about 10% by weight of the elastomer or epoxy materials have a molecular

weight less than about 1000. It is also contemplated that, for maintaining adhesive capability, components such as plasticizers or processing oils may be added to elastomer-based or epoxy-based materials and particularly to a thermoplastic-based material.

[00029] As general guidance for the material which receives the coating, it is preferable that at least 1% by weight of the components have a low enough molecular weight to be a liquid at about 23° C. More preferably, at least 5% by weight of the components have a low enough molecular weight to be a liquid at about 23° C. Still more preferably, at least 10% by weight of the components have a low enough molecular weight to be a liquid at about 23° C.

[00030] In most applications, it is undesirable for the underlying material itself be reactive at room temperature or otherwise at the ambient temperature in a manufacturing environment (e.g. up to about 40° C. or higher). More typically, the material becomes reactive at higher processing temperatures, such as those encountered in an automobile assembly plant. In such and embodiment, the material may be foamed upon automobile components at elevated temperatures or at higher applied energy levels, e.g., during painting preparation steps. While temperatures encountered in an automobile assembly operation may be in the range of about 148.89° C. to 204.44° C. (about 300° F. to 400° F.), body and paint shop applications are commonly about 93.33° C. (about 200° F.) or slightly higher. If needed, blowing agent activators can be incorporated into the base material to cause expansion at different temperatures outside the above ranges. Generally, suitable materials or foams for the material have a range of expansion ranging from approximately 0 to over 1000 percent.

[00031] Advantageously, the material of the present invention may be formed or otherwise processed in a variety of ways. For example, preferred materials can be processed by injection molding, extrusion, compression molding or with a robotically controlled extruder such as a mini-applicator. This enables the formation and creation of part designs that exceed the capability of most prior art materials.

[00032] In the event that the system described herein includes a reinforcing material, it may be an open mesh reinforcing material. The open mesh material of the present invention is at least partially open or has through-holes. It is contemplated that it may be advantageous to allow a significant portion of the underlying material to flow through the open portion and adhere to the vehicle structure that is opposite the open mesh layer. In a preferred embodiment, the open portion is at least about 25 percent of the area of layer 14, more preferably at least about 40 percent, and most preferably at least about 50 percent, but less than about 90 percent. It is

contemplated that the amount of area of the open portion be as high as possible while allowing the complete assembly to maintain its desired structural performance and physical properties.

[00033] The reinforcing material located onto the underlying material receiving the coating may include non-conductive threads or wire (e.g., elongated filament, fibrous, or fabric material), which may be applied as a mat, a cloth, a roving, a netting, a mesh, a scrim, or the like. In such embodiments, the strengthening material may be composed, for example, of woven or unwoven fibers, filaments or the like of cotton, glass (e.g., E-glass or S-glass), fiberglass, Mylar, nylon, polyester, carbon, aramid, plastics, polymers (e.g., thermoplastics such as polyamides (e.g., nylon), PET (e.g., Mylar), polycarbonate, polyethylene, polypropylene, polybutylene (e.g., polybutylene terephthalate), polystyrene, polyurethane, vinyl, or any combination thereof, or other materials. As used herein, "threads," or "wire" connotes a single filament of material, a braided bundle of filaments, or an unbraided bundle of filaments.

[00034] In other applications, it may appreciable that the reinforcing material may be bead-like particles, aggregates, hollow material (e.g., hollow particle), or otherwise, or any combination thereof. In such embodiments, the strengthening material may be composed, for example, of particles or the like of glass (e.g., E-glass or S-glass), fiberglass, nylon, polyester, carbon, aramid, plastics, polymers (e.g., thermoplastics such as polyamides (e.g., nylon), polycarbonate, polyethylene, polypropylene, polybutylene (e.g., polybutylene terephthalate), polystyrene, polyurethane, vinyl, or any combination thereof), or other materials.

[00035] As used herein, unless otherwise stated, the teachings envision that any member of a genus (list) may be excluded from the genus; and/or any member of a Markush grouping may be excluded from the grouping.

[00036] Unless otherwise stated, any numerical values recited herein include all values from the lower value to the upper value in increments of one unit provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component, a property, or a value of a process variable such as, for example, temperature, pressure, time and the like is, for example, from 1 to 90, preferably from 20 to 80, more preferably from 30 to 70, it is intended that intermediate range values such as (for example, 15 to 85, 22 to 68, 43 to 51, 30 to 32 etc.) are within the teachings of this specification. Likewise, individual intermediate values are also within the present teachings. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01, or 0.1 as appropriate. These are only examples of what is specifically intended and all possible combinations of numerical values between the lowest value and the highest value enumerated

are to be considered to be expressly stated in this application in a similar manner. As can be seen, the teaching of amounts expressed as "parts by weight" herein also contemplates the same ranges expressed in terms of percent by weight. Thus, an expression in the of a range in terms of “at least ‘x’ parts by weight of the resulting composition" also contemplates a teaching of ranges of same recited amount of "x" in percent by weight of the resulting composition."

[00037] Unless otherwise stated, all ranges include both endpoints and all numbers between the endpoints. The use of "about" or "approximately" in connection with a range applies to both ends of the range. Thus, "about 20 to 30" is intended to cover "about 20 to about 30", inclusive of at least the specified endpoints.

[00038] The disclosures of all articles and references, including patent applications and publications, are incorporated by reference for all purposes. The term "consisting essentially of to describe a combination shall include the elements, ingredients, components or steps identified, and such other elements ingredients, components or steps that do not materially affect the basic and novel characteristics of the combination. The use of the terms "comprising" or "including" to describe combinations of elements, ingredients, components or steps herein also contemplates embodiments that consist of, or consist essentially of the elements, ingredients, components or steps.

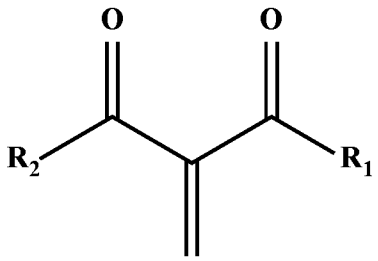
[00039] Plural elements, ingredients, components or steps can be provided by a single integrated element, ingredient, component or step. Alternatively, a single integrated element, ingredient, component or step might be divided into separate plural elements, ingredients, components or steps. The disclosure of "a" or "one" to describe an element, ingredient, component or step is not intended to foreclose additional elements, ingredients, components or steps.

[00040] It is understood that the above description is intended to be illustrative and not restrictive. Many embodiments as well as many applications besides the examples provided will be apparent to those of skill in the art upon reading the above description. The scope of the invention should, therefore, be determined not with reference to the above description, but should instead be determined with reference to the appended claims, along with the full scope of equivalents to which such claims are entitled. The disclosures of all articles and references, including patent applications and publications, are incorporated by reference for all purposes. The omission in the following claims of any aspect of subject matter that is disclosed herein is not a disclaimer of such subject matter, nor should it be regarded that the inventors did not consider such subject matter to be part of the disclosed inventive subject matter.

CLAIMS

What is claimed is:

1. A method comprising coating a polymeric material with a composition including a dicarbonyl compound represented by the formula

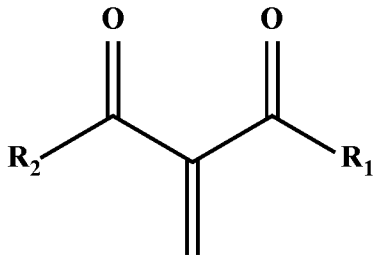


and having a viscosity of from about 50 cps to about 500 cps, wherein the coating initiates either: (i) spontaneous polymerization (e.g., in less than about one minute) at room temperature of the composition without the addition of an initiator; or (ii) polymerization at room temperature at a selected later time without the addition of an initiator; and wherein the composition adheres the polymeric material to a substrate.

2. The method of claim 1, wherein the substrate is metallic.
3. The method of claim 1 or claim 2, wherein one or more of the polymeric material and substrate are nucleophilic.
4. The method of any of the preceding claims, wherein the substrate, the polymeric material, or both have a pH of greater than 7.
5. The method of any of the preceding claims, wherein the coating step comprises applying a film to the polymeric material.
6. The method of any of the preceding claims, wherein the coating step includes spray coating, roll coating, brushing, dipping or any combination thereof.
7. The method of any of the preceding claims, wherein the composition forms a handling film.
8. The method of any of the preceding claims, wherein polymerization of the composition occurs at least 5 minutes, at least 15 minutes or even at least 30 minutes after coating.
9. The method of any of the preceding claims, wherein polymerization of the composition occurs less than 1 hour, less than 30 minutes, less than 15 minutes, or even less than 5 minutes after coating.

10. The method of any of the preceding claims, wherein the substrate is a sheet molding compound (SMC) material.
11. The method of any of the preceding claims, wherein the composition is stored in a container comprising one or more materials having a neutral pH and/or a pH of less than 7.
12. The method of any of the preceding claims, wherein the composition is formed as a paste.
13. The method of any of the preceding claims, wherein the composition includes a colorant.
14. The method of any of the preceding claims, wherein the polymeric material is formed with a bisphenol A precursor.
15. The method of any of the preceding claims, including welding the polymeric material after coating.
16. The method of any of the preceding claims, wherein the coated polymeric material is a tape.
17. The method of claim 15, wherein the tape includes a first surface containing a pressure sensitive adhesive formed by the coating and a second surface that is a heat activated adhesive.
18. The method of any of the preceding claims, wherein the coated polymeric material forms a laminate when applied to the substrate.
19. The method of any of the preceding claims, wherein the coated polymeric material is de-bonded and removed from the substrate.
20. The method of any of the preceding claims, wherein the composition is formed for locating into a glue gun application device.
21. The method of any of the preceding claims, wherein the composition is stored in a polyethylene container.
22. The method of any of the preceding claims, wherein the substrate is concrete.
23. The method of any of the preceding claims, wherein the substrate is coated with an oil-based substance.
24. The method of claim 23, wherein the oil-based substance is 61 MAL HCL 1.
25. The method of any of the preceding claims, wherein the coating forms a tack-free surface on the polymeric material.

26. The method of any of the preceding claims, including heating the coated polymeric material on the substrate to cause adhesion of the composition and/or polymeric material to the substrate.
27. The method of any of the preceding claims, wherein the polymeric material is a tacky material.
28. The method of any of the preceding claims wherein the polymeric material is a tack-free material.
29. The method of any of the preceding claims, wherein the polymeric material is an epoxy-containing material.
30. The method of any of the preceding claims, wherein the polymeric material includes an ethylene copolymer.
31. The method of any of the preceding claims, wherein the composition includes one or more of a diethyl, dimethyl, hexyl methyl, ethyl ethoxy ethyl, ethyl cyclohexyl, 2-phenylpropyl ethyl, dicyclohexyl, and fenchyl methyl.
32. The method of any of the preceding claims, wherein the polymeric material is a structural adhesive and the compositions increases dimensional stability of the adhesive.
33. The method of any of the preceding claims, wherein a reinforcing layer is added to the polymeric material and composition so that the reinforcing layer is: (i) located on the surface of the polymeric material; (ii) within (e.g., substantially surrounded by) the polymeric material; (iii) formed as a bead of extruded material; or (iv) any combination thereof.
34. The method of any of the preceding claims, wherein a reinforcing layer is added to the polymeric material and composition and the reinforcing layer comprises a scrim, a yarn, a fiber, a bead of solid epoxy-containing material, a weave, glass fibers, a mesh, or any combination thereof.
35. The method of any of the preceding claims, wherein one or more of the polymeric material or composition includes a thermoplastic epoxy component.
36. The method of any of the preceding claims, wherein a reinforcing layer is added to the polymeric material and composition and the reinforcing layer is a recyclable material.
37. The method of any of the preceding claims wherein the polymeric material is selected from a sealant, and adhesive, a patch, a tape, or any combination thereof.
38. A structure comprising a polymeric material, a composition including a dicarbonyl compound represented by the formula



coated onto the polymeric material and a substrate having a pH of greater than 7 located in contact with the composition.

39. The structure of claim 38, wherein the substrate is a metal.

40. The structure of claim 38 or claim 39, wherein one or more of the polymeric material and substrate are nucleophilic.

41. The structure of any of the preceding claims, wherein the substrate, the polymeric material, or both have a pH of greater than 7.

42. The structure of any of the preceding claims, wherein the coating step comprises applying a film to the polymeric material.

43. The structure of any of the preceding claims, wherein the coating step includes spray coating, roll coating, brushing, dipping or any combination thereof.

44. The structure of any of the preceding claims, wherein the composition forms a handling film.

45. The structure of any of the preceding claims, wherein polymerization of the composition occurs at least 5 minutes, at least 15 minutes or even at least 30 minutes after coating.

46. The structure of any of the preceding claims, wherein polymerization of the composition occurs less than 1 hour, less than 30 minutes, less than 15 minutes, or even less than 5 minutes after coating.

47. The structure of any of the preceding claims, wherein the substrate is a sheet molding compound (SMC) material.

48. The structure of any of the preceding claims, wherein the composition is stored in a container comprising one or more materials having a neutral pH and/or a pH of less than 7.

49. The structure of any of the preceding claims, wherein the composition is formed as a paste.

50. The structure of any of the preceding claims, wherein the composition includes a colorant.

51. The structure of any of the preceding claims, wherein the polymeric material is formed with a bisphenol A precursor.

52. The structure of any of the preceding claims, including welding the polymeric material after coating.

53. The structure of any of the preceding claims, wherein the coated polymeric material is a tape.

54. The structure of claim 53, wherein the tape includes a first surface containing a pressure sensitive adhesive formed by the coating and a second surface that is a heat activated adhesive.

55. The structure of any of the preceding claims, wherein the coated polymeric material forms a laminate when applied to the substrate.

56. The structure of any of the preceding claims, wherein the composition is formed for locating into a glue gun application device.

57. The structure of any of the preceding claims, wherein the composition is stored in a polyethylene container.

58. The structure of any of the preceding claims, wherein the substrate is concrete.

59. The structure of any of the preceding claims, wherein the substrate is a vehicle panel.

60. The structure of any of the preceding claims, wherein the substrate is coated with an oil-based substance.

61. The structure of claim 60, wherein the oil-based substance is 61 MAL HCL 1.

62. The structure of any of the preceding claims, wherein the coating forms a tack-free surface on the polymeric material.

63. The structure of any of the preceding claims, including heating the coated polymeric material on the substrate to cause adhesion of the composition and/or polymeric material to the substrate.

64. The structure of any of the preceding claims, wherein the polymeric material is a tacky material.

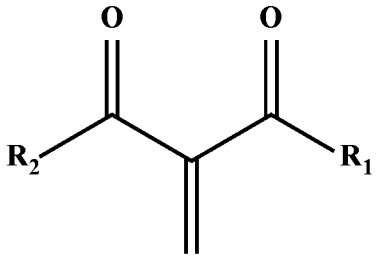
65. The structure of any of the preceding claims wherein the polymeric material is a tack-free material.

66. The structure of any of the preceding claims, wherein the polymeric material is an epoxy-containing material.

67. The structure of any of the preceding claims, wherein the polymeric material includes an ethylene copolymer.

68. The structure of any of the preceding claims, wherein the composition includes one or more of a diethyl, dimethyl, hexyl methyl, ethyl ethoxy ethyl, ethyl cyclohexyl, 2-phenylpropyl ethyl, dicyclohexyl, and fenchyl methyl.

69. A method comprising coating a polymeric material with a composition including a dicarbonyl compound represented by the formula



and having a viscosity of from about 50 cps to about 500 cps, wherein the coating polymerizes upon the addition of an initiator and wherein the composition adheres the polymeric material to a substrate.

70. An automotive reinforcing device for use in a vehicle comprising:

an expandable polymeric material;

an open mesh located in direct planar contact with the expandable material and along the entirety of the expandable material, wherein the expandable material is tacky prior to expansion allowing the expandable material to adhere to the open mesh; and

a malonate handling film disposed on at least a portion of the expandable material and the open mesh, wherein the malonate handling film is configured to allow the automotive reinforcing device to adhere to a surface of the vehicle.

71. The automotive reinforcing device of claim 70, wherein the device is configured to conform to the shape of the surface.

72. The automotive reinforcing device of claim 70 or claim 71, wherein the device is flexible (e.g., capable of easily bending without breaking).

73. The automotive reinforcing device of any of claims 70 through 72, wherein the device will bend under its own weight when held at its end.

74. The automotive reinforcing device of any of claims 70 through 73, wherein the volumetric activation of the activatable material is at least about 100% and less than about 300%.

75. The automotive reinforcing device of any of claims 70 through 74, wherein the expandable material includes a structural adhesive material.

76. The automotive reinforcing device of any of claims 70 through 75, wherein the expandable material includes a sealant material.

77. The automotive reinforcing device of any of claims 70 through 76, wherein the open mesh has an open area of at least 50 percent of a total surface area and the malonate handling film is adapted so that polymerization occurs at the time the automotive reinforcing device contacts the surface of the vehicle.

78. The automotive reinforcing device of any of claims 70 through 77, wherein the malonate handling film is adapted so that polymerization occurs at the time the automotive reinforcing device contacts the surface of the vehicle

79. A method for structurally reinforcing a vehicle body stamping comprising:

forming a tacky expandable structural adhesive material;

locating an open mesh material onto the expandable material;

applying a handling film to the tacky expandable structural adhesive material and to the open mesh material forming an automotive reinforcing device;

contacting the automotive reinforcing device with a surface of the vehicle body stamping;

initiating polymerization of the handling film;

activating the expandable material to expand by application of heat;

wherein the automotive reinforcing device remain in contact with the stamping surface by means of the tacky nature of the expandable material prior to activating the expandable material, the handling film, or both.

80. The method of claim 79, wherein the method is free of any separate fastening step for connecting the automotive reinforcing device to the body stamping.

81. The method of claim 79 or claim 80, including flexing the automotive reinforcing device to conform to the shape of the body stamping prior to activating the expandable material.

82. The method of any of claims 79 through 81, including cutting the expandable material to a desired shape prior to locating the open mesh onto the expandable material.

83. The method of any of claims 79 through 82, including cutting the automotive reinforcing device to a desired shape prior to contacting the automotive reinforcing device with the vehicle body stamping surface.

84. The method of any of claims 79 through 83, wherein the step of forming the tacky expandable structural adhesive material is free of any molding process.

85. The method of any of claims 79 through 84, wherein the step of locating the open mesh onto the expandable material is free of any separate fastening step for connecting the open mesh to the expandable material.

86. The method of any of claims 79 through 85, wherein the step of activating the expandable material includes volumetric expansion of at least about 100% and less than about 300%.

87. The method of any of claims 79 through 86, including flexing the automotive reinforcing device so that a first portion of the automotive reinforcing device is arranged at an angle of 90° or less from a second portion of the automotive reinforcing device.

88. The method of any of claims 79 through 87, including flexing the automotive reinforcing device so that a surface of the vehicle body stamping is contacted by the automotive reinforcing device that would not be contacted by the automotive reinforcing device if automotive reinforcing device were substantially rigid.

89. The method of any of claims 79 through 88, wherein the open mesh is located onto the expandable material so that the expandable material substantially covers the open mesh and is free of any voids on the open mesh that are not covered with the expandable material prior to activation.

90. The method of any of claims 79 through 89, wherein the automotive reinforcing device are no longer flexible after activation of the expandable material.

91. The method of any of claims 79 through 90, wherein the automotive reinforcing device continue to be flexible after activation of the expandable material.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/028853

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09J4/00 C09D167/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09J C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 160 864 A (PONTICELLO IGNAZIO S ET AL) 10 July 1979 (1979-07-10) column 2, line 37 - column 3, line 5; claims 1-5; examples 1-6	1-69
X	US 9 217 098 B1 (STEVENSON PETER RULON [US] ET AL) 22 December 2015 (2015-12-22) column 4, line 23 - column 5, line 38; claims 1-20	1-69
X	WO 2013/149165 A1 (BIOFORMIX INC [US]) 3 October 2013 (2013-10-03) claims 1-40	69

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 July 2017	27/09/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Sperry, Pascal

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/028853

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-69

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-69

A method comprising coating a polymeric material with a composition including a specific dicarbonyl compound and having a viscosity of from 50 cps to 500 cps, and wherein the composition adheres the polymeric material to a substrate. A structure comprising a polymeric material, a composition including a specific dicarbonyl compound coated onto the polymeric material and a substrate having a pH of greater than 7 located in contact with the composition.

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2. claims: 70-91

An automotive reinforcing device for use in a vehicle comprising: an expandable polymeric material;
an open mesh located in direct planar contact with the expandable material and along the entirety of the expandable material, wherein the expandable material is tacky prior to expansion allowing the expandable material to adhere to the open mesh; and a malonate handling film disposed on at least a portion of the expandable material and the open mesh, wherein the malonate handling film is configured to allow the automotive reinforcing device to adhere to a surface of the vehicle.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/028853

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4160864 A	10-07-1979	CA 1088090 A	21-10-1980
		DE 2734082 A1	16-03-1978
		FR 2363615 A1	31-03-1978
		GB 1556558 A	28-11-1979
		JP S5331740 A	25-03-1978
		JP S5757067 B2	02-12-1982
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		EP 2831125 A1	04-02-2015
		JP 6188252 B2	30-08-2017
		JP 2015512460 A	27-04-2015
		US 2015073110 A1	12-03-2015
		WO 2013149165 A1	03-10-2013