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(71) Applicant: **HUNTSMAN INTERNATIONAL LLC** [US/US]; 10003 Woodloch Forest Drive, The Woodlands, Texas 77380 (US).

(72) Inventors: **PRIEMEN, Stefan**; Grijpenlaan 18, 3300 Tienen (BE). **PRATELLI, Daniele**; Grijpenlaan 18, 3300 Tienen (BE). **LEROY, Dimitri**; Grijpenlaan 18, 3300 Tienen (BE).

(74) Agent: **ROBERTS, Philippa**; Grijpenlaan 18, 3300 Tienen (BE).

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(54) Title: MULTI-COATING SYSTEM FOR COMPOSITE VESSELS

(57) Abstract: The present disclosure provides a multi-coating system operable to provide an impact protective coating and a fire protective coating to various substrates, such as a composite vessel. The multi-coating system generally includes an impact protective coating composition including a polyisocyanate component and a polyisocyanate reactive composition and a fire protective coating composition including an isocyanate component, an isocyanate-reactive hydrogen composition and an intumescent component.

MULTI-COATING SYSTEM FOR COMPOSITE VESSELS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of EP23181639.8 filed 27 June 2023. The contents of the same are incorporated herein by reference.

FIELD

[0002] The present disclosure is generally directed to a multi-coating system with impact resistance and passive fire protection properties useful in various applications, such as providing external protection to a composite vessel.

BACKGROUND

[0003] Generally, pressure vessels are structures capable of containing a fluid, e.g., liquids, liquefied gases, compressed gases, and combinations thereof, under pressure. Exemplary pressure vessels include storage containers (e.g., fuel tanks, portable gas (e.g., oxygen) storage bottles, and accumulators) as well as pipes and other conduits that may be used to transport fluids at elevated pressures (e.g., hydraulic lines) and structures exposed to transient elevated pressures (e.g., rocket motor casings and launch tubes).

[0004] Traditionally, pressure vessels were made of metal. While many factors affect material selection (e.g., thermal stability, corrosion resistance, and fatigue performance) decreasing the weight, improving the burst strength, and increasing the useful life have become significant factors for pressure vessel designers. These demands have led to an increased use of fiber-reinforced composites in the construction of pressure vessels. However, an important disadvantage of such vessels is that the fiber-reinforced composite materials can be easily damaged by impact and also do not perform well at low and high temperatures and are not resistant to fire.

[0005] One approach to improve performance at low and high temperature is to coat the composite material with a protective coating and an intumescent coating for the protection to fire. Conventional intumescent coatings used for passive fire protection include water-based acrylic systems that perform well for fire protection but may have very long drying times and may

exhibit no or very limited mechanical strength once they have dried. Therefore, such coatings may not form a protective layer against impact. Epoxy resin systems have also been used to provide fire protection properties. While performing extremely well in connection with fire protection requirements, they require several hours to dry, may need to be heated to accelerate the reticulation process and have limited low temperature flexibility. Because both systems suffer from less than acceptable mechanical properties, chemical product exposure may also become an issue if the coating is damaged due to impact thereby exposing the composite material's external surface to chemical attack from the atmosphere and foreign matter.

[0006] Thus, there is a need for an inexpensive way in which to protect composite vessels and/or to produce composite vessels providing both impact resistance and passive fire protection.

SUMMARY

[0007] The present disclosure is generally directed to a multi-coating system capable of withstanding impact from extraneous objects as well as exposure to fire and high temperature, and as such can be applied to a composite vessel or other substrates to protect the composite vessel or substrate from impact damage, chemical exposure and fire. According to one embodiment, the multi-coating system comprises: (i) an impact protective coating composition comprising a polyisocyanate component and a polyisocyanate reactive composition; and (ii) a fire protective coating composition selected from an epoxy adhesive, a polyurethane elastomer, and an intumescent-containing composition comprising (a) an organic thermosetting component, (b) a curing agent for the organic thermosetting component, and (c) an intumescent component. In various embodiments, the organic thermosetting component may include, but is not limited to, an epoxy resin, a benzoxazine resin, an acrylic or methacrylic resin, an organopolysiloxane resin, a polyisocyanate (which can be the same or different as the polyisocyanates in the polyisocyanate component for the impact protective coating composition) or combinations thereof and the curing agent may include, but is not limited to, an amine, thiol, carboxylic acid, anhydride, and/or a polyhydric alcohol.

DETAILED DESCRIPTION

[0008] The present disclosure generally provides a multi-coating system and its use in connection with the protection of composite vessels. The multi-coating system of the present disclosure is capable of providing both a passive fire protection layer and an impact protection layer, such layers being applied in series to the external surface of the composite vessel. Both layers are capable of curing/drying quickly (i.e., are tack free in less than about 10 seconds, or less than about 5 seconds, such as about 2 seconds, and develop about 80%-90% of their final properties within about 15-30 minutes) thus reducing manufacturing time as well as capital expenditure needs (e.g., reduced need for drying ovens) and energy costs (i.e., reduced heat required for curing/drying). Furthermore, by combining an impact protection (damping) layer underneath (or above) a more rigid fire protection layer, the fire protection layer is damaged less during any impact, especially at low temperature, versus when used without. The damping layer may also form an extra shield against chemical product ingress.

[0009] If appearing herein, the term "comprising" and derivatives thereof are not intended to exclude the presence of any additional component, step, or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound, unless stated to the contrary. In contrast, the term, "consisting essentially of" if appearing herein, excludes from the scope of any succeeding recitation any other component, step, or procedure, except those that are not essential to operability and the term "consisting of", if used, excludes any component, step or procedure not specifically delineated or listed. The terms "or" and “and/or”, unless stated otherwise, refer to the listed members individually as well as in any combination. For example, the expression A and/or B refers to A alone, B alone, or to both A and B.

[0010] The articles "a" and "an" are used herein to refer to one or to more than one (i.e., to at least one) of the grammatical objects of the article. By way of example, "a polyisocyanate" means one polyisocyanate or more than one polyisocyanate. The phrases "in one embodiment", "according to one embodiment" and the like generally mean the particular feature, structure, or characteristic following the phrase is included in at least one embodiment of the present disclosure, and may be included in more than one embodiment of the present disclosure.

Importantly, such phrases do not necessarily refer to the same embodiment. If the specification states a component or feature "may", "can", "could", or "might" be included or have a characteristic, that particular component or feature is not required to be included or have the characteristic.

[0011] The terms “preferred” and “preferably” refer to embodiments that may afford certain benefits, under certain circumstances. However, other embodiments may also be preferred, under the same or other circumstances. Furthermore, the recitation of one or more preferred embodiments does not imply that other embodiments are not useful, and is not intended to exclude other embodiments from the scope of the present disclosure.

[0012] The term “about” as used herein can allow for a degree of variability in a value or range, for example, it may be within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range.

[0013] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but to also include all of the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range such as from 1 to 6, should be considered to have specifically disclosed sub-ranges, such as, from 1 to 3, from 2 to 4, from 3 to 6, etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

[0014] The term “optional” or “optionally” means that the subsequently described event or circumstance may or may not occur, and that the description includes instances where said event or circumstance occurs and instances where it does not.

[0015] “Isocyanate index” or “NCO index” or “index” refers to the ratio of NCO-groups over isocyanate-reactive hydrogen atoms present in a formulation, given as a percentage: [NCO]x100/[active hydrogen] (%). In other words, the NCO-index expresses the percentage of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically required for reacting with the amount of isocyanate reactive hydrogens used in a formulation. It should be observed that the isocyanate index as used herein is considered from the point of view

of the actual reaction process involving the isocyanate ingredients and the isocyanate-reactive ingredients. Any isocyanate groups consumed in a preliminary step to produce modified polyisocyanates (including such isocyanate derivatives referred to in the art as prepolymers) or any active hydrogens consumed in a preliminary step (e.g., reacted with isocyanate to produce modified polyols or polyamines) are not taken into account in the calculation of the isocyanate index. Only the free isocyanate groups and the free isocyanate-reactive hydrogens (including those of the water) present at the actual reaction stage are taken into account.

[0016] The expression "isocyanate-reactive hydrogens" as used herein for the purpose of calculating the isocyanate index refers to the total of active hydrogen atoms in hydroxyl and amine groups present in the compositions; this means that for the purpose of calculating the isocyanate index of the actual reaction process, one hydroxyl group is considered to comprise one reactive hydrogen, one primary amine group is considered to comprise one reactive hydrogen and one water molecule is considered to comprise two active hydrogens.

[0017] The term "reaction system" refers to a combination of components where the polyisocyanates are kept in one or more containers separate from the isocyanate-reactive hydrogen components.

[0018] The term "multi-coating system" refers to a combination of components where the individual coating compositions are kept in one or more containers separate from each other.

[0019] The term "composite vessel" is used herein in its ordinary sense and refers to a hollow or concave item, typically sealable, for holding fluids or other contents and comprising a composite material.

[0020] The term "composite material" refers to an assembly of structural fibers and a binder or matrix material. Structural fibers may be organic fibers, inorganic fibers or mixtures thereof, including for example commercially available structural fibers such as carbon fibers, glass fibers, aramid fibers (e.g., Kevlar), high-modulus polyethylene (PE) fibers, polyester fibers, poly-p-phenylene-benzobisoxazole (PBO) fibers, quartz fibers, alumina fibers, zirconia fibers, silicon carbide fibers, other ceramic fibers, basalt, natural fibers and mixtures thereof. It is noted that end uses that require high-strength composite structures would typically employ fibers having a

high tensile strength (e.g., ≥3500 MPa or ≥500 ksi). Such structural fibers may include one or multiple layers of fibrous material in any conventional configuration, including for example, unidirectional tape (uni-tape) webs, non-woven mats or veils, woven fabrics, knitted fabrics, non-crimped fabrics, fiber tows and combinations thereof. It is to be understood that structural fibers may be included as one or multiple plies across all or a portion of the composite material, or in the form of pad-ups or ply drops, with localized increases/decreases in thickness.

[0021] The fibrous material is held in place and stabilized by a binder or matrix material, such that alignment of the fibrous material is maintained and the stabilized material can be stored, transported and handled (e.g., shaped or otherwise deformed) without fraying, unraveling, pulling apart, buckling, wrinkling or otherwise reducing the integrity of the fibrous material.

[0022] The binder or matrix material is generally selected from thermoplastic polymers, thermoset resins, and combinations thereof. Thermoplastic polymers include, for example, polyesters, polyamides, polyimides, polycarbonates, poly(methyl methacrylates), polyaromatics, polyesteramides, polyamideimides, polyetherimides, polyaramides, polyarylates, polyaryletherketones, polyetheretherketones, polyetherketoneketones, polyacrylates, poly(ester) carbonates, poly(methyl methacrylates/butyl acrylates), polysulphones, polyarylsulphones, copolymers thereof and combinations thereof. Thermoset materials include, for example, epoxy resins, bismaleimide resins, formaldehyde-condensate resins (including formaldehyde-phenol resins), cyanate resins, isocyanate resins, phenolic resins and mixtures thereof. The epoxy resin may be mono or poly-glycidyl derivative of one or more compounds selected from the group consisting of aromatic diamines, aromatic monoprimary amines, aminophenols, polyhydric phenols, polyhydric alcohols, and polycarboxylic acids. The epoxy resins may also be multifunctional (e.g., di-functional, tri-functional, and tetra-functional epoxies).

[0023] The term “coating” refers to a film or layer formed from a coating composition of the present disclosure, without regard to the thickness of the film or layer, and further includes cured, partially cured, and wet coatings (that is, coatings that have not been at least partially or fully cured).

[0024] The term "hydroxyl value" refers to the concentration of hydroxyl groups, per unit weight of the polyol, that are able to react with the isocyanate groups. The hydroxyl number is reported as mg KOH/g, and may be measured according to the standard ASTM D 1638.

[0025] The term "average functionality", or "average hydroxyl functionality" of a polyol indicates the number of OH groups per molecule, on average. The average functionality of an isocyanate refers to the number of -NCO groups per molecule, on average.

[0026] The term "substantially free" refers to a composition in which a particular constituent or moiety is present in an amount that has no material effect on the overall composition. In some embodiments, "substantially free" may refer to a composition in which the particular constituent or moiety is present in the composition in an amount of less than about 5 wt.%, or less than about 4 wt.%, or less than about 3 wt.% or less than about 2 wt.% or less than about 1 wt.%, or less than about 0.5 wt.%, or less than about 0.1 wt.%, or less than about 0.05 wt.%, or even less than about 0.01 wt.% based on the total weight of the composition, or that no amount of that particular constituent or moiety is present in the respective composition.

[0027] The present disclosure generally provides a multi-coating system providing both impact resistance and passive fire protection properties and is suitable for the external protection of composite vessels. In an embodiment, the multi-coating system includes: (i) an impact protective coating composition comprising a polyisocyanate component; and a polyisocyanate reactive composition comprising one or more polyamines or one or more polyhydric alcohols or a mixture thereof; and (ii) a fire protective coating composition selected from an epoxy adhesive, a polyurethane elastomer, and an intumescent-containing composition comprising (a) an isocyanate component, (b) an isocyanate-reactive hydrogen composition including one or more compounds containing an isocyanate-reactive hydrogen, and (c) an intumescent component.

[0028] According to one embodiment, the polyisocyanate component in the impact protective coating composition includes one or more polyisocyanates such as an aliphatic polyisocyanate or an aromatic polyisocyanate.

[0029] Examples of aliphatic polyisocyanates include, but are not limited to, hexamethylene diisocyanate (HDI), tetraalkyl xylene diisocyanate, cyclohexane diisocyanate,

1,12-dodecane diisocyanate, 1,4-tetramethylene diisocyanate, 1,3- and 1,4-cyclohexane diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethyl-cyclohexane (isophorone diisocyanate), 4,4'-, 2,2'- and 2,4'-dicyclohexyl-methane diisocyanate, as well as the corresponding isomer mixtures.

[0030] Examples of aromatic polyisocyanates include but are not limited to, m-phenylene diisocyanate, p-phenylene diisocyanate, 4,4'- or 2,4'- or 2,2'-diphenylmethane diisocyanate (MDI), polymethylene polyphenylene diisocyanate (mixtures of MDI and oligomers thereof known in the art as "crude" or polymeric MDI having an isocyanate functionality of greater than 2), 2,4- and 2,6-toluene diisocyanate (TDI), dianisidine diisocyanate, bitolylene diisocyanate, naphthalene-1,4-diisocyanate and diphenylene 4,4'-diisocyanate.

[0031] Alternatively, semi-prepolymers or prepolymers formed from the reaction of a polyisocyanate (e.g., methylene diphenyl diisocyanate (MDI), modified MDI and/or p-MDI) with a polyhydric alcohol may also be employed as the polyisocyanate. The polyhydric alcohol may be a polyether polyol, a polyester polyol, a polycarbonate polyol, a polycaprolactone polyol, or other polyol. These polyols may be used either individually or in combinations of two or more. In addition, the polyhydric alcohol may be a copolymer of one or more of a polyether polyol, a polyester polyol, a polycarbonate polyol, a polycaprolactone polyol, or other polyol. In one embodiment, the polyhydric alcohol is a copolymer of a polyester polyol and a polycarbonate polyol.

[0032] Examples of polyether polyols include, but are not limited to, polyethylene glycol, polypropylene glycol, polypropylene glycol-ethylene glycol copolymer, polytetramethylene glycol, polyhexamethylene glycol, polyheptamethylene glycol, polydecamethylene glycol, and polyether polyols obtained by ring-opening co-polymerization of alkylene oxides, such as ethylene oxide and/or propylene oxide, with isocyanate-reactive initiators of functionality from 2 to 8. The isocyanate-reactive initiators include, but are not limited to, alcohols, glycols or high molecular weight polyether polyols.

[0033] Polyester polyols include, but are not limited to, those which may be obtained by reacting a diol and a polybasic acid. Examples of diols include ethylene glycol, polyethylene glycol, tetramethylene glycol, polytetramethylene glycol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, 1,9-

nonanediol and 2-methyl-1,8-octanediol. Examples of polybasic acids include phthalic acid, dimer acid, isophthalic acid, terephthalic acid, maleic acid, fumaric acid, adipic acid and sebacic acid.

[0034] Examples of polycarbonate polyols include, but are not limited to, aliphatic polycarbonate diols, for example those based upon alkylene glycols, ether glycols, alicyclic glycols or mixtures thereof. In some embodiments, the alkylene groups for preparing the polycarbonate polyol can comprise from 5 to 10 carbon atoms and can be a straight chain, cycloalkylene or combinations thereof. Non-limiting examples of such alkylene groups include hexylene, octylene, decylene, cyclohexylene and cyclohexyldimethylene. The polycarbonate polyols can be prepared, in non-limiting examples, by reacting the alkylene glycol with a dialkyl carbonate, such as methyl, ethyl, n-propyl or n-butyl carbonate, or diaryl carbonate, such as diphenyl or dinaphthyl carbonate, or by reacting a hydroxy-terminated alkylene diol with phosgene or bischoloroformate, in a manner well known to those skilled in the art.

[0035] Polycaprolactone polyols include, but are not limited to, those prepared by condensing caprolactone in the presence of an initiator such as water, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, dipropylene glycol, 1,3-propylene glycol, polyethylene glycol, polypropylene glycol, poly(oxyethylene-oxypropylene)glycols and similar polyalkylene glycols, either blocked, capped or heteric containing up to about 40 or more alkyleneoxy units in the molecule, 3-methyl-1,5-pentanediol, cyclohexanediol, 4,4'-methylene-bis-cyclohexanol, 4,4'-isopropylidene bis-cyclohexanol, xylenediol, 2-(4-hydroxymethylphenyl)ethanol, 1,4- butanediol, glycerol, trimethylolpropane, 1,2,6-hexanetriol, triethanolamine, triisopropanolamine, erythritol, pentaerythritol and N,N,N',N'-tetrakis-(2-hydroxyethyl)ethylene diamine. The caprolactone reacted with the initiator can be caprolactone itself or a substituted caprolactone as described in US Pat. No. 3169945, the contents of which are herein incorporated by reference.

[0036] Examples of other polyols may include ethylene glycol, propanediols, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, cyclohexanedimethanol, polyoxyethylene bisphenol A ether, polyoxypropylene bisphenol A ether, polyoxyethylene bisphenol F ether, and polyoxypropylene bisphenol F ether.

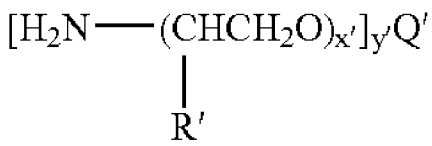
[0037] In one embodiment, the polyisocyanate is a prepolymer having an NCO value from about 8% to about 31% or from about 12% to about 25%, or from about 16% to about 20% that is obtained from MDI, optionally uretonimine-modified and a polypropylene glycol (in some embodiments having a molecular weight from about 1500-2500 Daltons ("Da").

[0038] In one embodiment, the polyisocyanate is a prepolymer having an NCO value from about 8% to about 31% or from about 10% to about 25%, or from about 12% to about 20% that is obtained from MDI, optionally uretonimine-modified and a polypropylene glycol (in some embodiments having a molecular weight from about 1500-2500 Daltons ("Da")).

[0039] According to one embodiment, the polyisocyanate reactive composition includes one or more polyamines alone or optionally blended with one or more polyhydric alcohols. In other embodiments the polyisocyanate reactive composition includes one or more polyhydric alcohols alone or optionally blended with one or more polyamines. The polyhydric alcohol can be any of the polyhydric alcohols described above in relation to the production of semi-prepolymers and prepolymers. According to one embodiment, the amount of the one or more polyhydric alcohols is less than about 50% by weight, based on the total weight of polyhydric alcohols and polyamines, and in some embodiments between about 5% by weight and about 15% by weight, based on the total weight of polyhydric alcohols and polyamines. In another embodiment, the amount of the one or more polyhydric alcohols is about 50% by weight to about 100% by weight, based on the total weight of the polyhydric alcohols and polyamines. In some embodiments when the one or more polyhydric alcohols are used alone (i.e., they are used at 100% by weight, based on the total weight of polyhydric alcohols and polyamines), the amount of the one or more polyhydric alcohols present in the polyisocyanate reactive composition may be about 30% by weight to about 90% by weight, or about 50% by weight to about 70% by weight, based on the total weight of the polyisocyanate reactive composition.

[0040] In one embodiment, the polyamine is a polyoxyalkylene polyamine. The polyoxyalkylene polyamine can be a primary and/or secondary amine-terminated polyether polyol typically having a weight average molecular weight of more than about 100 Da, such as from about 200-5000 Da; a functionality of from 2 to 6, such as from 2 to 3; and an amine

equivalent weight of from about 750-4000 g/eq. In another embodiment, the polyoxyalkylene polyamine is a compound having the formula



where Q' is the polyvalent residue of an isocyanate-reactive hydrogen-containing compound used as an initiator after removal of at least one isocyanate reactive hydrogen and y' is at least 2, such as 2 to 8 or 2 to 3. Each R' is independently hydrogen, methyl, ethyl or propyl. The R' groups are preferably hydrogen and/or methyl, including their mixtures. The average number of oxyalkylene repeating units per amine, given by x', is at least 1, such as from about 1 to about 40, or from about 1 to about 10.

[0041] Initiators may include, but are not limited to, one or more diols such as ethylene glycol, propylene glycol, 1,2- or 1,4-butanediol or triols, such as trimethylolpropane and glycerine. In some embodiments, preferred initiators include ethylene glycol, propylene glycol, trimethylolpropane and glycerine. Typical oxyalkylene repeating units include oxyethylene, oxypropylene and oxybutylene, including mixtures thereof. When two or more oxyalkylenes are used, they may be present in any form, such as randomly or in blocks. Examples of particular polyoxyalkylene polyamines include JEFFAMINE® brand polyoxyalkylene polyamines, such as diamines D-230, D-400, D-2000, D-4000, SD-231, SD-401 and XTJ-576 and triamines T-403, T-3000, T-5000 and ST-404.

[0042] In one embodiment, when the polyamines are used alone (i.e., they are used in an amount of 100% by weight, based on the total weight of the polyamines and polyhydric alcohols) the total amount of polyamines present in the polyisocyanate reactive composition may range up to about 75% by weight, such as from about 40% by weight to about 75% by weight, or from about 45% by weight to about 65% by weight, or from about 50% by weight to about 60% by weight based on the total weight of the polyisocyanate reactive composition. In other embodiments, the total amount of polyamines may be less than about 40% by weight, or less than about 35% by weight, or less than about 30% by weight, or less than about 25% by weight, or less than about

20% by weight, or less than 15% by weight, or less than about 10% by weight, based on the total weight of the polyisocyanate reactive composition.

[0043] The polyisocyanate reactive composition can also include an amine-terminated chain extender. The amine-terminated chain extender may be, but is not limited to: 1-methyl-3,5-diethyl-2,4- or 2,6-diaminobenzene (also called diethyltoluene diamine or DETDA); 1,3,5-triethyl-2,6-diaminobenzene; 3,5,3',5'-tetraethyl-4,4'-diaminodiphenylmethane; di(methylthio)-toluene diamines including 3,5-di(methylthio)-2,4 and 2,6-toluene diamine; N,N'-bis(t-butyl)ethylene diamine; 4,4'-methylenebis(2-isopropyl-6-methylaniline); 4,4'-methylenebis(2,6-diisopropylaniline; isophorone diamine; guanamines as described in WO 2004/090009 in particular 2,4-diamino-6-nonyl-1,3,5-triazine; 4,4'-methylene-bis(3-chloro-2,6-diethylaniline); aceto amino trimethyl cyclohexane methanamine; and mixtures thereof.

[0044] The total amount of the amine-terminated chain extender may range from about 5% by weight to about 45% by weight, or from about 10% by weight to about 25% by weight, based on the total weight of the polyisocyanate reactive composition. In other embodiments, the total amount of the amine-terminated chain extender may range from about 20% by weight to about 45% by weight, or from about 25% by weight to about 30% by weight, based on the total weight of the polyisocyanate reactive composition.

[0045] The polyisocyanate component and the polyisocyanate reactive composition may react to form the impact protective coating without the aid of a catalyst. However, if desired, a catalyst can be used, such as an organic tin compound or a tertiary amine. The organic tin compound may be a stannous or stannic compound, such as a stannous salt of a carboxylic acid, a trialkyltin oxide, a dialkyltin dihalide, a dialkyltin oxide, where the organic groups of the organic portion of the tin compound are hydrocarbon groups containing from 1 to 8 carbon atoms. For example, dibutyltin dilaurate, dibutyltin diacetate, diethyltin diacetate, dihexyltin diacetate, di-2-ethylhexyltin oxide, dioctyltin dioxide, stannous octoate, stannous oleate, or a mixture thereof, may be used. Tertiary amine catalysts include trialkylamines (e.g., trimethylamine, triethylamine); heterocyclic amines such as N-alkylmorpholines (e.g., N-methylmorpholine, N-ethylmorpholine), 2,2'-dimorpholinodiethyl ether, 1,4-dimethylpiperazine; and aliphatic polyamines such as N,N,N',N'-tetramethyl-1,3-butanediamine, dimethyldiaminodiethylether and triethylenediamine.

Examples of other catalysts which may be present include, but are not limited to, bismuth, cobalt, zirconium and zinc salts.

[0046] One or more additives may also be included in the polyisocyanate component or the polyisocyanate reactive composition. Examples include, but are not limited to: functional alkoxy silanes, such as those described in U.S. Pat. No. 5731397, the contents of which are herein incorporated by reference, to improve adhesion or other adhesion promoters; wetting agents; levelling agents; viscosity-controlling additives, (corrosion protection) pigments, color pigments or dyes; UV absorbers/stabilizers; antioxidants; water scavengers; thixotropic agents or rheology modifiers; plasticizers; surfactants; defoaming agents; nucleating agents (e.g., nano clays); antimicrobial agents; reinforcing material, for example, chopped or milled glass fibers, chopped or milled carbon fibers and/or mineral fibers; and organic and inorganic fillers.

[0047] In some embodiments, the relative amount of polyisocyanate to polyoxyalkylene polyamine and chain extender is any amount sufficient to make the impact protective coating. Typically, from about 0.7 to about 1.6, or from about 0.8 to about 1.3, or from about 1.05 to about 1.25 moles of polyisocyanate are provided per moles of amine.

[0048] The components of the impact protective coating composition may be blended together, e.g., using high speed dispersion equipment. The weight percentage, mole percentage or volume percentage of starting components will vary depending upon the equipment utilized, the starting components activities and the desired coating's characteristics. In one embodiment, a reaction system useful to produce the impact protective coating includes component A (polyisocyanate component) and component B (polyisocyanate reactive composition) and comprises from about 30% by weight to about 70% by weight component A and from about 70% by weight to about 30% by weight component B, or from about 40 by weight to about 60% by weight component A and from about 60% by weight to about 40% by weight component B, or an about 5050% by weight mixture of component A and component B.

[0049] In some embodiments, the impact protective coating composition reacts to form an impact protective coating having a glass transition temperature of less than about -30°C, or less than about -35°C or less than about -40°C, or less than about -50°C. In some embodiments, less than about -60°C. In other embodiments, the impact protective coating composition reacts such

that the impact protective coating comprises a thermoplastic polyurethane or a polyurea or a polyurethane or a polyurea/polyurethane.

[0050] The multi-coating system also includes (ii) a fire protective coating composition selected from an epoxy adhesive, a polyurethane elastomer, and an intumescent-containing composition comprising (a) an isocyanate component, (b) an isocyanate-reactive hydrogen composition including one or more compounds containing an isocyanate-reactive hydrogen, and (c) an intumescent component.

[0051] In one embodiment, the epoxy adhesive includes at least one epoxide compound with an epoxide functionality of at least 1 and at least one epoxide hardener.

[0052] Any organic compound having an oxirane ring polymerizable by a ring opening reaction may be used as the epoxide compound including monomeric epoxy compounds and polymeric epoxy compounds which can be aliphatic, cycloaliphatic, aromatic or heterocyclic. In some embodiments, the epoxide compound generally has at least two polymerizable epoxy groups per molecule and, more preferably, from two to four polymerizable epoxy groups per molecule.

[0053] The epoxide compound may vary from low molecular weight monomeric products to high molecular weight polymers and may also vary greatly in the nature of the backbone and any substituent groups. The molecular weight may vary from about 58 Daltons to about 100,000 Daltons or more. The backbone may be of any type and may be essentially halogen-free and, in particular, chlorine-free. It may also be brominated. Any substituents can also be essentially halogen-free or brominated and may otherwise be any group not having a nucleophilic or an electrophilic moiety (such as active hydrogen atom) that is reactive with an oxirane ring. Substituents include ester groups, ether groups, sulfonate groups, siloxane groups, nitro groups, amide groups, nitrile groups, phosphate groups, etc. Mixtures of various epoxide compounds may also be used.

[0054] In one embodiment, the epoxide compound(s) are preferably derived from bisphenol A, bisphenol E, bisphenol F, bisphenol S, aliphatic and aromatic amines, such as methylene dianiline and aminophenols, and halogen substituted bisphenol resins, novolacs,

aliphatic epoxies, and any combinations thereof. In another embodiment, the epoxide compound is selected from a diglycidyl ether of bisphenol A, a diglycidyl ether hydrogenated bisphenol A, a diglycidyl ether of bisphenol F, a diglycidyl ether of hydrogenated bisphenol F, an epoxy novolac, a cycloaliphatic epoxy, and a mixture thereof.

[0055] The epoxide hardeners which may be used are materials that react with the oxirane ring of the epoxide compound to cause substantial crosslinking of the epoxide. These materials contain at least one nucleophilic or electrophilic moiety (such as an active hydrogen atom) that cause the crosslinking reaction to occur. Examples include, but are not limited to, aliphatic amines, aromatic amines, aliphatic acid anhydrides, aromatic acid anhydrides, alicyclic acid anhydrides, polyamides, imidazoles, amine complexes, amine derivatives, phenols and mixtures thereof.

[0056] In another embodiment, the fire protective coating composition is a thermoplastic polyurethane elastomer. The polyurethane elastomer may be prepared using a polyol, including any of the polyhydric alcohols described herein, a polyisocyanate, including any of the polyisocyanates described herein, and a chain extender. Examples of the polyols include polyester polyols, polyester ether polyols, polycarbonate polyols, polyether polyols and mixtures thereof.

[0057] In one embodiment, the polyol is a polyester polyol including those obtained by dehydration condensation between an aliphatic dicarboxylic acid (e.g., succinic acid, adipic acid, sebacic acid, or azelaic acid), an aromatic dicarboxylic acid (e.g., phthalic acid, terephthalic acid, isophthalic acid, or naphthalenedicarboxylic acid), an alicyclic dicarboxylic acid (e.g., hexahydrophthalic acid, hexahydroterephthalic acid, or hexahydroisophthalic acid), or an acidic ester or anhydride thereof and ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, 1,3-octanediol, 1,9-nonanediol, or a like polyol, or a mixture of these polyols; and polylactone diols obtained by ring-open polymerization of a lactone monomer, such as ϵ-caprolactone.

[0058] In another embodiment, the polyol is a polyester ether polyol, including polyester ether polyols include those obtained by dehydration condensation between an aliphatic dicarboxylic acid (e.g., succinic acid, adipic acid, sebacic acid, or azelaic acid), an aromatic

dicarboxylic acid (e.g., phthalic acid, terephthalic acid, isophthalic acid, or naphthalenedicarboxylic acid), an alicyclic dicarboxylic acid (e.g., hexahydrophthalic acid, hexahydroterephthalic acid, or hexahydroisophthalic acid), or an acidic ester or anhydride thereof and a glycol, such as diethylene glycol or a propylene oxide adduct, or a mixture of these glycols.

[0059] In another embodiment, the polyol is a polycarbonate polyol including those obtained by the reaction between at least one polyhydric alcohol (e.g., ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, 1,8-octanediol, 1,9-nonanediol, or diethylene glycol) and diethylene carbonate, dimethyl carbonate and diethyl carbonate.

[0060] In still another embodiment, the polyol is a polyether polyol including polyethylene glycol, polypropylene glycol, and polytetramethylene ether glycol, which are each obtained by polymerization of a cyclic ether (e.g., ethylene oxide, propylene oxide, and tetrahydrofuran, respectively), and their copolyethers.

[0061] In some embodiments, the polyisocyanate is tolylene diisocyanate (TDI), 4,4'-diphenylmethane diisocyanate (MDI), 1,5-naphthalene diisocyanate (NDI), tolidine diisocyanate, 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), xylylene diisocyanate (XDI), hydrogenated XDI, triisocyanate, tetramethylxylene diisocyanate (TMXDI), 1,6,11-undecane triisocyanate, methyloctane 1,8-diisocyanate, lysine ester triisocyanate, 1,3,6-hexamethylene triisocyanate, bicycloheptane triisocyanate, and dicyclohexylmethane diisocyanate (hydrogenated MDI, or HMDI). Preferred among them are 4,4'-diphenylmethane diisocyanate (MDI), 1,6-hexamethylene diisocyanate (HDI) and mixtures thereof.

[0062] The chain extender may be a low molecular weight polyol. Examples of the low molecular polyol include aliphatic polyols, such as ethylene glycol, 1,3-propylene glycol, 1,2-propylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, 1,8-octanediol, 1,9-nonanediol, diethylene glycol, 1,4-cyclohexanedimethanol, and glycerol; and aromatic glycols, such as 1,4-dimethyrolbenzene, bisphenol A, and bisphenol A ethylene oxide or propylene oxide adducts.

[0063] Examples of some polyurethane elastomer types include ester-based (lactone-based) polyurethane copolymers, ester-based (adipate-based) polyurethane copolymers, ether-based polyurethane copolymers, carbonate-based polyurethane copolymers, and ether/ester-based polyurethane copolymers. Examples of commercially available ester-based (lactone-based) polyurethane copolymers include Elastollan C80A10 (from BASF Corp.), Elastollan C80A50 (from BASF Corp.) and Resamine P-4000 and P-4500 series (from Dainichiseika Color & Chemicals Mfg. Co., Ltd.). Examples of commercially available ester-based (adipate-based) polyurethane copolymers include Pandex T-5000V (DIC Bayer Polymer Ltd.), Pandex TR-3080 (from DIC Bayer Polymer Ltd.), and Resamine P-1000 and P-7000 series (from Dainichiseika Color & Chemicals Mfg. Co., Ltd.). Examples of commercially available ether-based polyurethane copolymers include Elastollan 1180A50 (from BASF Corp.), Pandex T-8180 (from DIC Bayer Polymer Ltd.), Pandex T-8283 (from DIC Bayer Polymer Ltd.), Pandex T-1190 (from DIC Bayer Polymer Ltd.), and Resamine P-2000 series (from Dainichiseika Color & Chemicals Mfg. Co., Ltd.). Examples of commercially available carbonate-based polyurethane copolymers include Pandex T-7890N (from DIC Bayer Polymer Ltd.). Examples of commercially available ether/ester-based polyurethane copolymers include Desmopan DesKU2-88586 (from DIC Bayer Polymer Ltd.) and Resamine P-800 series (from Dainichiseika Color & Chemicals Mfg. Co.). These elastomers can be used alone or in any combination.

[0064] In another embodiment, the fire protective coating composition is an intumescent-containing composition comprising (a) an isocyanate component, (b) an isocyanate-reactive hydrogen composition including one or more compounds containing an isocyanate-reactive hydrogen, and (c) an intumescent component.

[0065] The isocyanate component can include a polyisocyanate, including any of the polyisocyanates described above in relation to the impact protective coating composition. In one embodiment, the polyisocyanate may be toluene diisocyanate (TDI), a diphenylmethane diisocyanate (MDI)-type isocyanate, or a semi-prepolymer or prepolymer of these diisocyanates. In some embodiments, the polyisocyanate may have at least two aromatic rings in its structure, and is a liquid product. MDI-type isocyanates and derivatives thereof having a functionality greater than 2, such as about 2.1-2.2, are preferred. The diphenylmethane diisocyanate (MDI) can be in the form of its 2,4'-, 2,2'- and 4,4'-isomers and mixtures thereof, the mixtures of

diphenylmethane diisocyanates (MDI) and oligomers thereof known in the art as "crude" or polymeric MDI (polymethylene polyphenylene polyisocyanates) having an isocyanate functionality of greater than 2, or any of their derivatives having a urethane, isocyanurate, allophonate, biuret, uretonimine, uretdione and/or iminooxadiazinedione groups and mixtures of the same.

[0066] Examples of other suitable polyisocyanates include hexamethylene diisocyanate (HMDI), isophorone diisocyanate (IPDI), butylene diisocyanate, trimethylhexamethylene diisocyanate, di(isocyanatocyclohexyl)methane, isocyanatomethyl-1,8-octane diisocyanate and tetramethylxylene diisocyanate (TMXDI).

[0067] The semi-prepolymers and prepolymers can include those obtained by reacting polyisocyanates with the polyhydric alcohols described above, mercaptans, carboxylic acids, amines, urea, amides or amino functional silanes (such as described in WO 2010/131037, the contents of which are incorporated herein by reference). In particular embodiments, the prepolymers are those obtained by reacting polyhydric alcohols having a molecular weight of from about 400-5000 Da with excess quantities of polyisocyanates. In another particular embodiment the prepolymers used as the polyisocyanate component have an average functionality of about 2.0 to about 2.9, or about 2.1 to about 2.5, a maximum viscosity up to about 35000 mPa s, such as between about 30000-35000 mPa s, or about 6000 mPa s, and an isocyanate content of about 6% by weight to about 30% by weight, or about 16% by weight to about 25% by weight.

[0068] The isocyanate-reactive hydrogen composition includes one or more compounds containing an isocyanate-reactive hydrogen. The compound containing an isocyanate-reactive hydrogen may be any of the polyhydric alcohols or polyamines described above. In one embodiment, the compound containing an isocyanate-reactive hydrogen includes a polyester polyol, a polycarbonate polyol, a polycaprolactone polyol, a polytetramethylene ether glycol (PTMEG), an amine derivative of these polyols or any mixture of two or more of these compounds.

[0069] In one embodiment, the polyfunctional polycarbonate polyol can be obtained by reacting a polyhydric alcohol with a carbonyl component selected from the group consisting of phosgene, a chloroformate, a dialkylcarbonate, a diarylcarbonate, an alkylene carbonate and a mixture thereof. In another embodiment, the polycarbonate polyol is a polycaprolactone and

polycarbonate block co-polymer polyol. The polycarbonate polyol preferably has 2 hydroxyl groups in one molecule and has a number average molecular weight from about 200-5000 Da, or from about 400-1000 Da and has a hydroxyl value from about 20-850, or from about 100-350. Higher functional (more than 2 or even more than 3) polycarbonate polyols can also be used.

[0070] In some embodiments, the polyhydric alcohol used for preparation of the polycarbonate polyol can be a straight chain diol, a branched diol, a triol or higher hydric (4 to 6 hydric) alcohol, or a mixture thereof. Examples of straight chain diols include 1,3-propylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexane diol, 1,8-octane diol, 1,9-nonane diol and 1,10-decanediol. Examples of branched diols are 2 methyl-1,3-propanediol, 3-methyl-1,5-pentanediol, neopentyl glycol, 2,2-diethyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 2,2-diethyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 2-methyl-1,8-octanediol, 2,2,4-trimethyl-1,3-pentanediol, 2-ethyl-1,3-hexanediol and 1,4-cyclohexane dimethanol. The tri- or higher hydric alcohols include: triols, such as glycerine, trimethylol ethane and trimethylol propane; tetraols, such as trimethylol propane dimer, pentaerythritol and 1,2,7,8-octane tetraol; pentaols such as ribitol, arabitol and xylitol; and hexaols such as sorbitol, allitol, mannitol, dulcitol and pentaerythritol dimer.

[0071] In some embodiments, the polycarbonate polyol may have carboxyl groups with an acid value less than 50. The polycarbonate polyol containing such carboxyl groups is obtained by reacting the polycarbonate polyol with an acid anhydride or a dicarboxylic acid at a temperature from about 120°-180°C. The acid anhydride may be phthalic anhydride, trimelitic anhydride, tetrahydro-phthalic anhydride, succinic anhydride and itaconic anhydride and the dicarboxylic acid may be adipic acid, sebacic acid, phthalic acid and isophthalic acid.

[0072] The polycaprolactone polyols may have an average molecular weight from about 290-6000 Da, or from about 290-3000 Da, or from about 300-1000 Da. The average hydroxyl number of the polycaprolactone polyol can be from about 15-600, or from about 150-500, and the polycaprolactone polyol can have an average of from about 2 to about 6, or from about 2 to about 4 hydroxyl groups.

[0073] The PTMEG's are generally synthesized by a ring-opening chain extension reaction of monomeric tertrahydrofuran (THF). In one well-known method, the ring-opening reaction is

catalyzed by fluorosulfonic acid, followed by hydrolysis of sulfate ester groups and water extraction of the acid, followed by neutralization and drying. In many cases, the PTMEG will be solid at room temperature because of its high degree of crystallinity. In the event one desires to employ a room temperature liquid PTMEG, the THF can be copolymerized with alkylene oxides (also known as cyclic ethers or monoepoxides) as described in US Pat. No. 4211854, incorporated herein by reference Such copolymers have an A-B-A block-heteric structure, where the A blocks are random copolymers of tetrahydrofuran and alkylene oxides and the B block is made up of polytetramethylene oxides.

[0074] The cyclic ethers co-polymerizable with tetrahydrofuran are not particularly limited, provided that they are cyclic ethers capable of ring-opening polymerization, and may include, for example, 3-membered cyclic ethers, 4-membered cyclic ethers, cyclic ethers such as tetrahydrofuran derivatives, and cyclic ethers such as 1,3-dioxolan and trioxane. Examples of cyclic ethers include ethylene oxide, 1,2-butene oxide, 1,2-hexene oxide, 1,2-t-butyl ethylene oxide, cyclohexene oxide, 1,2-octene oxide, cyclohexylethylene oxide, styrene oxide, phenyl glycidyl ether, allyl glycidyl ether, 1,2-decene oxide, 1,2-octadecene oxide, epichlorohydrin, epibromohydrin, epiiodohydrin, perfluoropropylene oxide, cyclopentene oxide, 1,2-pentene oxide, propylene oxide, isobutylene oxide, trimethyleneethylene oxide, tetramethyleneethylene oxide, styrene oxide, 1,1- diphenylethylene oxide, epifluorohydrin, 1,1,1-trifluoro-2-propylene oxide, 1,1,1-trifluoro-2-methyl-2-propylene oxide, 1,1,1-trichloro-2-methyl-3-bromo-2-propylene oxide, 1,1,1-tribromo-2-butyleneoxide, 1,1,1-trifluoro-2-butyleneoxide, 1,1,1-trichloro-2-butylene oxide, oxetane, 3-methyloxetane, 3,3-dimethyloxetane, 3,3-diethyloxetane, 3,3-bis(chloromethyl)oxetane, 3,3-bis(bromomethyl)oxetane, 3,3-bis(iodomethyl)oxetane, 3,3-bis(fluoromethyl)oxetane, 2-methyltetrahydrofuran, 3-methyltetrahydrofuran, 2-methyl-3-chloromethyltetrahydrofuran, 3-ethyltetrahydrofuran, 3-isopropyltetrahydrofuran, 2-isobutyl-tetrahydrofuran and 7-oxabicyclo(2,2,1)heptane.

[0075] The content of the copolymerized cyclic ether, if present, in the PTMEG may be within the range of from about 5% by weight to about 95% by weight, based on the total weight of the PTMEG. Additionally, in the synthesizing reaction of PTMEG, a part of the starting THF may be replaced with an oligomer of PTMEG as the starting material. Further, in the synthesizing reaction of a copolymerized polyetherglycol, an oligomer of PTMEG or an oligomer of the

polyetherglycol to be synthesized may also be added as a part of the starting material to carry out the reaction.

[0076] In some embodiments the PTMEG has a number average molecular weight from about 600-6000 Da, or from about 1000-4000 Da, or form about 1300-3000 Da.

[0077] The isocyanate component and isocyanate-reactive hydrogen composition may constitute from about 20% by weight to about 90% by weight of the intumescent-containing composition. In other embodiments the isocyanate component and isocyanate-reactive hydrogen composition constitutes from about 30% by weight to about 60% by weight of the intumescent-containing composition.

[0078] The intumescent-containing composition also includes an intumescent component. The intumescent component generally contains at least one or more intumescent ingredients containing phosphorus, nitrogen and boron atoms with a weight ratio of phosphorus to nitrogen in the intumescent component being between 0.5/1 to 1.5/1 and the amount of boron being from about 1% by weight to about 5% by weight, based on the total weight of the fire protective coating composition. The intumescent component is typically provided in the form of an intumescent filler composition which may comprise two or more intumescent ingredients, which together result in intumescence. The intumescent filler composition (which may alternatively be referred to as an "intumescent filler package") for use in the present disclosure may contain at least one or more intumescent ingredients containing phosphorus (P), nitrogen (N) and boron (B) atoms. These might be different intumescent ingredients, each one containing either P, N or B or one or more intumescent ingredients can contain two or more of P, N and/or B.

[0079] According to the present disclosure the weight ratio of phosphorus atoms to nitrogen atoms present in the intumescent filler composition may be between about 0.5/1 to about 1.5/1, or between about 0.8/1 to about 1/1 or between about 0.7/1 to about 0.9/1, or between about 0.6/1 to about 1/1. Further the weight percentage of boron atoms in the intumescent-containing composition may be from about 1% by weight to about 5% by weight, or from about 1% by weight to about 3.5% by weight, or from about 1% by weight to about 2.5% by weight, based on the total weight of the intumescent-containing composition. In another embodiment, the weight ratio of phosphorus and nitrogen atoms to boron atoms in the

intumescent filler composition is between about 10/1 to about 0.5/1, or between about 7/1 to about 2/1, or between about 6/1 to about 3/1, or between about 6/1 to about 4/1.

[0080] Apart from the compounds containing P, N and/or B atoms, the intumescent filler composition may contain other intumescent ingredients. For example, the intumescent filler composition may include an acid source selected from, for example, ammonium polyphosphate, melamine polyphosphate, magnesium sulphate, boric acid, a phosphorus containing polyol, dihydroxaphosphaphenanthrene oxide and an adduct thereof.

[0081] In one embodiment, the preferred acid source is ammonium polyphosphate. Ammonium polyphosphate can vary in molecular weight (chain length), the lower the molecular weight, the higher its solubility. By having very high molecular weight and a crosslinked structure it is possible to have very low water solubility, though higher thermal stability is generally observed. Coating ammonium polyphosphate with silane, melamine or melamine formaldehyde may be beneficial in further reducing solubility and can also lead to higher loadings due to a reduction in resin absorbing properties. The use of coated ammonium polyphosphate is preferred, and ammonium polyphosphate coated with melamine formaldehyde is most preferred. In some embodiments, the acid source is present in an amount from about 20% by weight to about 50% by weight, based on the total weight of the intumescent component.

[0082] Additional customary carbon sources, such as polyhydric alcohols (pentaerythritol and dipentaerythritol) are generally not needed but may be present. Starch and expandable graphite are other possible carbon sources. Any additional carbon source, if present, preferably is present in an amount from about 5 by weight to about 40% by weight, or from about 15% by weight to about 25% by weight, based on the total weight of the intumescent component.

[0083] The intumescent component may also include a gas source. The gas source may include melamine, melem, melon, melamine orthophosphate, melamine polyphosphate, melamine pyrophosphate, dimelamine pyrophosphate, melamine phosphate, melamine borate, melamine formaldehyde, melamine cyanurate, tris-(hydroxyethyl) isocyanurate (THEIC), ethylenediamine phosphate, piperazine phosphate, piperazine polyphosphate, ammonium polyphosphate, 1,3,5-triglycidyl isocyanurate, triallyl isocyanurate and mixtures thereof, and chlorinated paraffin. The preferred gas source is melamine (which is not considered when

calculating the isocyanate index) or a derivative thereof preferably containing nitrogen or phosphorus. In some embodiments, the gas source is present in an amount from about 5% by weight to about 40% by weight, or from about 6% by weight to about 15% by weight, based on the total weight of the intumescent component.

[0084] It will be understood that one ingredient may supply more than one function of the intumescent ingredients. Thus, melamine phosphate could be the acid source and the gas source; or the boron containing compound could be the acid source and the gas source; or the resin binder could be the carbon source and the gas source, as well as being a major component of the polymer coating. When one component supplies more than one function, the component may be present in an amount selected from any definition herein, applying to the relevant function. For example, melamine phosphate may be present as an acid source and as a gas source in an amount from about 5% by weight to about 60% by weight of the intumescent-containing composition. More preferably, in such a situation where one component supplies more than one function, the component is present in an amount satisfying each definition herein, applying to the relevant functions. For example, melamine phosphate is most preferably present in an amount from about 20% by weight to about 40% by weight of the intumescent-containing composition.

[0085] Examples of boron-containing compounds to be used in the intumescent filler composition include: alkali metal borates, such as borax decahydrate, borax pentahydrate, disodium octaborate tetrahydrate, anhydrous borax, sodium metaborate, potassium tetraborate, potassium pentaborate; boric acid and boric oxide; alkaline earth metal borates, such as calcium borate, magnesium borate, barium metaborate; transition metal borates, such as zinc borates, aluminum borate, manganese borate, silver borate, iron borate, copper borate, nickel borate, strontium borate, lead borate, zirconium borate; boron and nitrogen-containing compounds, such as ammonium tetraborate, ammonium pentaborate, melamine diborate, guanidium borate, boron nitride, borazine; borester and boron-carbon compounds, such as boric acid esters, boric acid ester salts, boronic acid, boron carbide; boron and phosphorus-containing compounds, such as boron phosphate, phosphine-borane; boron and silicon-containing compounds, such as borosilicate, borosilicate glass, frits, borosiloxane; layered double hydroxides with borate; fluoroborates. Preferred compounds are ammonium tetraborate and ammonium pentaborate. According to particular embodiments boric acid and/or boric oxides are not present in the

intumescent component (e.g., the intumescent-containing composition is substantially free of boric acid, boric oxides or boric acid and boric oxides).

[0086] The boron-containing compound may be present in an amount of from about 10% by weight to about 60% by weight, based on the total weight of the intumescent component.

[0087] Although not an essential ingredient in intumescent reactions, inorganic "nucleating" agents are sometimes included since they promote sites for the intumescent char to form and improve the thermal resistance properties and stability of the intumescent char during a fire. The intumescent component may contain at least one nucleating agent, examples of which include titanium dioxide, zinc oxide, aluminium oxide, silica, fumed silica, silicates such as magnesium silicate, potassium silicate, sodium silicate, calcium silicate, aluminium silicate, calcium magnesium silicate (talc) and zeolites, heavy metal oxides such as cerium oxide, lanthanum oxide and zirconium oxide, mica and bentonite clay. A preferred nucleating agent is titanium dioxide which also provides opacity to the coating. The nucleating agent may be present in an amount from about 1% by weight to about 25% by weight, or from about 15% by weight to about 20% by weight, based on the total weight of the intumescent component. More preferably the nucleating agent may be present in an amount from about 1% by weight to about 10% by weight or from about 5% by weight to about 10 % by weight, based on the total weight of the intumescent component.

[0088] Optional additives may also be included as part of the intumescent ingredient to aid char formation and to strengthen the char and prevent char degradation. Such additives include solids such as zinc borate, zinc stannate, zinc hydroxystannate, glass flake, glass spheres, polymeric spheres, fibres (ceramic, mineral, glass/silica based), aluminium hydroxide, antimony oxide, boron phosphate, fumed silica and expandable graphite.

[0089] In one embodiment, an intumescent filler package, based on the total weight of the intumescent component, for use in the present disclosure (and which may be present in the fire protective coating composition in an amount from about 30% by weight to about 50% weight on total weight of the intumescent-containing composition) includes: titanium dioxide (about 10%-20% by weight); ammonium pentaborate (tetrahydrate) (about 10%-60% by weight); ammonium polyphosphate (about 20%-40% by weight); and melamine (about 5%-40% by weight).

[0090] In some embodiments, the intumescent component is present in an amount from about 10% by weight to about 90% by weight, based on the total weight of the intumescent-containing composition. In other embodiments, the intumescent component is present in amount from about 30% by weight to about 70% by weight or from about 40% by weight to about 50% by weight, or from about 40% by weight to about 60% by weight, or from about 40% by weight to about 70% by weight, based on the total weight of the intumescent-containing composition.

[0091] Generally, the intumescent component is also present in an amount such that the intumescent-containing composition is capable of swelling to at least three times, or at least five times, or at least ten times, its original volume when exposed to temperatures found in a typical fire situation. The temperature in a fire can be anywhere in the range from about 150°-1000°C and it is preferred that the composition starts to intumesce at a temperature in the lower part of this range. The reference temperature for measurement of swelling can be taken to be 500°C.

[0092] Typically, the intumescent-containing composition swells to more than 300%, preferably more than 1000%, more preferably more than 5000% of its original thickness when in the form of a coating and exposed to heat at a temperature of 500°C. For instance, the intumescent-containing composition may be applied to a substrate to form a layer approximately 1 mm thick after curing. Upon exposure to heat at a temperature of about 500°C this may swell to a thickness in the range 5 mm to 10 mm.

[0093] The polymerization reaction of the intumescent-containing composition generally takes place at an isocyanate index of about 60%-150%, such as about 80%-130% and can take place in the presence or absence of a catalyst. Any of the catalysts described above may be used. Examples of preferred catalysts include dibutyltin dilaurate or any other organo-metal catalyst such as bismuth, cobalt, zinc or zirconium-based catalysts. The amount of the catalyst used may be from about 0.005%-5% by weight, based on the weight of the intumescent-containing composition.

[0094] In some embodiments an amine-terminated chain extender, such as those described above, may be present to make the setting faster. Other known additives which may be optionally added to the intumescent composition includes levelling agents, viscosity-controlling

additives, (corrosion protection) pigments, color pigments or dyes, fillers, matting agents, UV absorbers/stabilizers, antioxidants, water scavengers, thixotropic agents or rheology modifiers, reinforcing agents, plasticizers, surfactants, adhesion promotors (e.g., silanes), defoaming agents, nucleating agents (e.g., nano clays) and antimicrobial agents. These additives may be present in amounts ranging from about 0.01%-25% by weight of the intumescent-containing composition. In some embodiments, the intumescent-containing composition is substantially free of halogens.

[0095] In order that the fire protective coating composition can be applied at high film thickness by multiple passes without intermediate cure it may be preferred to modify the rheology of the fire protective coating composition by the incorporation of a thixotrope. Suitable thixotropic additives include organically modified inorganic clays such as bentonite clays, hectorite clays or attapulgite clays, organic wax thixotropes based on castor oil and fumed silica. The most preferred thixotropic additives are wax thixotropes and fumed silicas. The thixotropic additive may be present in an amount from about 0%-2% by weight, such as from about 0.05%-1.5% by weight of the fire protective coating composition.

[0096] To improve or facilitate dispersion of the intumescent ingredients and also to reduce the overall viscosity of the intumescent-containing composition, it may be necessary to incorporate wetting/dispersion additives. Such additives are usually liquid in form and can be supplied either containing a solvent or are solvent free. Where required preferably a solvent free wetting agent is used, even more preferably a wetting agent with acid functionality is recommended, at levels from about 0%-2% by weight of the intumescent-containing composition.

[0097] The fire protective coating composition may also comprise a solvent (e.g., xylene) to reduce viscosity and improve the sprayability of the composition. However, according to some embodiments the fire protective coating composition is substantially free of a solvent. The fire protective coating composition may also comprise a plasticizer which has the function of softening and extending the final cured polymer network and providing extra liquid components so that the mineral fillers are fully wetted-out.

[0098] The (a) organic thermosetting component, (b) curing agent for the organic thermosetting component and (c) intumescent component of the intumescent-containing composition may be blended together using high speed dispersion equipment. For example, the

solid intumescent components of component (c) may be wetted out and dispersed in the other components (a) and (b). As with the impact protective coating composition, the fire protective coating composition may be a reaction system supplied in more than one component which may be mixed prior to use. The individual components, will, when mixed, undergo chemical reactions to cause the molecular weight to rise. Preferably in one embodiment where the (a) organic thermosetting component is the isocyanate component and the (b) curing agent component is the isocyanate-reactive hydrogen composition, all of the intumescent component (c) is added to the isocyanate-reactive hydrogen composition (component (b)) but at high loading (> 50% by weight) it may be necessary to put part of component of (c) in the isocyanate component (component (a)). For example, the nucleating agent (e.g., TiO_2) or the N and/or P-containing compound (e.g., ammonium polyphosphate) or part thereof can be pre-mixed with the (a) isocyanate component; generally the amount of intumescent component (c) pre-mixed with the (a) isocyanate component varies between 0% and about 75% by weight, or from about 10% by weight to about 50% by weight, based on total weight of component (a) (containing the polyisocyanates of the isocyanate component) and the nucleating agent or the N and/or P-containing compound or part thereof and no component (b).

[0099] If premixed, the boron containing intumescent ingredient of component (c) is always added to the (b) isocyanate-reactive hydrogen composition component; generally, the amount of boron containing intumescent ingredient pre-mixed with the (b) isocyanate-reactive hydrogen composition varies from about 15% by weight to 70% by weight, based on total weight of component (b) (containing the isocyanate-reactive hydrogen compounds of the isocyanate-reactive hydrogen composition and the boron-containing intumescent ingredient and no component (a)).

[00100] According to another embodiment, there is a provided a process for producing a cured impact resistant intumescent substrate. In the case where each of the impact protective coating composition and the fire protective coating composition of the present disclosure are two-part compositions this process includes the steps of (a) applying a first part (e.g., polyisocyanate component) of a two-part impact protective coating composition and a second part (e.g., polyisocyanate reactive composition) of the two-part impact protective coating composition to at least a portion of a surface of a substrate, (b) allowing the first part and the

second part to cure by allowing a reaction between the first part and the second part to proceed to form an impact protective coating on the surface of the substrate; (c) applying a first part (e.g., isocyanate component) of a two-part fire protective coating composition and a second part (e.g., isocyanate-reactive hydrogen composition and intumescent component) of the two-part fire protective coating composition to at least a portion of the impact protective layer; and (d) allowing the first part and the second part to cure by allowing a reaction between the first part and the second part to proceed to form a fire protective coating on the impact protective coating.

[00101] In an alternative embodiment, the process includes the steps of (a) applying a first part of a two-part fire protective coating composition and a second part of the two-part fire protective coating composition to at least a portion of a surface of a substrate, (b) allowing the first part and the second part to cure by allowing a reaction between the first part and the second part to proceed to form a fire protective coating on the surface of the substrate; (c) applying a first part of a two-part impact protective coating composition and a second part of the two-part impact protective coating composition to a portion of the fire protective coating and (d) allowing the first part and the second part to cure by allowing a reaction between the first part and the second part to proceed to form an impact protective coating on the fire protective coating.

[00102] The impact protective and fire protective coating compositions may be applied to the substrate, or in some embodiments an adhesive that has been applied to the substrate, to form a coating thereon by a variety of techniques including, but not limited to, casting, (electrostatic) spraying, brushing, dipping, and pouring. These and other application techniques are well known to those skilled in the art. The coating compositions may be such that they can be coated onto a surface, and remain in place, as the polymeric coating forms. When applied, each may suitably be a liquid, or a formable material, for example a gel, mastic, or paste. Each may comprise one or more solid components, and thus may be a suspension or dispersion.

[00103] Thus, in an embodiment each of the impact protective coating composition and the fire protective coating composition includes a first part and a second part (i.e., polyisocyanate component and polyisocyanate reactive composition for the impact protective coating composition and the organic thermosetting component, curing agent component and intumescent component (for the fire protective coating composition). The first part and second

part of the impact protective coating composition and the first part and second part of the fire protective coating composition are mixed together prior to their application to a substrate. Preferably this pre-mixing occurs very shortly before application to the substrate, for example, a few seconds before application in an on-line mixer incorporated into an airless spraying apparatus, or by means of any other spraying apparatus conventionally used to mix and apply two component coatings to substrates (e.g., impingement mixing or static mixing guns). The compositions will be understood as curing under ambient conditions after application, although a heated forced air or a heat cure can be applied to accelerate final cure or to enhance coating properties such as adhesion.

[00104] In one embodiment, airless spray is the preferred application. Airless spray pumps having a ratio of 45:1 or greater, and preferably 60:1 are suitable. A minimum hydraulic pressure of greater than 150 bar, such as from about 170 bar to about 250 bar, is required and the compositions are sprayed using a tip size ranging from 0.015 inch to 0.045 inch. In some embodiments, the mean thickness of each of the coatings may be from about 1 mm to about 45 mm, or from about 2 mm to about 25 mm, or in some embodiments less than about 10 mm.

[00105] In accordance with another embodiment of the present disclosure there is provided a method of coating an external surface of a composite vessel for protection against damage from impact and during a fire situation, the method comprising the steps of applying the impact protective coating composition around (on top of) the composite vessel and allowing it to form an impact protective coating and applying the fire protective coating composition around (on top of) the impact protective coating and allowing it to form a fire protective coating around (on top of) the impact protective coating. Alternatively, the process may include the steps of applying the fire protective coating composition around (on top of) the composite vessel and allowing it to form a fire protective coating and applying the impact protective coating composition around (on top of) the fire protective coating and allowing it to form an impact protective coating around (on top of) the fire protective coating. The composite vessel may comprise a structural matrix comprising fibers, typically carbon fibers, and a thermoplastic resin or thermosetting resin. Examples of thermoplastic resins are as described above, for example, they include, but are not limited to, polyethylene, polypropylene, polyvinylidene fluoride, and ethylene chloro trifluoro

ethylene. Examples of thermosetting resins are as described above, for example, they include, but not limited to, polyester, vinylester, epoxy and polyurethane.

[00106] In an embodiment, there is provided a coated composite vessel made by the method or by the process described above.

[00107] In an embodiment, there is provided a substrate with a surface, wherein at least a portion of the surface is coated with an impact protective coating and a fire protective coating coated onto at least a portion of the impact protective coating. The nature of the impact protective coating and the fire protective coating are as described above.

[00108] Non-limiting examples of other substrates on which the multi-coating system may be applied to (on an internal surface and/or external surface) include, but are not limited to, metal, natural and/or synthetic stone, ceramic, glass, brick, cement, concrete, cinderblock, wallboard, drywall, sheetrock, cement board, plastic, paper, PVC, roofing materials such as shingles, roofing composites and laminates, and roofing drywall, styrofoam, plastic composites, acrylic composites, ballistic composites, asphalt, fiberglass, soil and gravel. Metals can include but are not limited to aluminum, cold rolled steel, electrogalvanized steel, hot dipped galvanized steel, titanium and alloys; plastics can include but are not limited to thermoplastic polyolefin materials, sheet moulding compound or composite, polypropylene, polycarbonate, polyethylene, and polyamides (Nylon). In some particular embodiments, the multi-coating system of the present disclosure may be used in connection with a hydrogen storage tank or battery. In still another embodiment, the multi-coating system of the present disclosure may be used in connection with the protection of wood, e.g., a structural wood assembly such as cross laminated timber.

[00109] Examples

[00110] Materials and Methods

- Commercially available two-component epoxy coating system for cellulosic fire protection.

- Huntsman supplied intumescent coating A as described in WO2015/052148 (the contents of which are incorporated herein by reference), comprising an MDI prepolymer with NCO = 15%, EQW=282, MW ~564.

- Huntsman supplied fast curing PU coating, Tg ~ -40°C to -60°C, NCO = 15%, EQW=282, MW ~564.

Metal sheets of 3mm thick were sandblasted to create a surface roughness of SA2 ½. Coatings were then applied with a thickness of approximately 2mm as described below. Material plates were stored for at least one week at 25 °C before being submitted to impact testing.

Dynamic Impact testing according to ISO6603-1:2000 was performed. Briefly, each metal plate was placed onto solid steel block with a thickness of 5cm. The temperature of the experimental set up was reduced in a Votsch climate chamber. An impact testing weight was dropped onto the sample. The impact energy was 30.0 kJ.

Each test was repeated five times.

The surface damage was assessed using the criteria in Table 1. A low score indicates good impact protection. A high score indicates poor impact protection. For example, if a sample shows splitting cracks in the top coat which propagate through to the base coat exposing the surface of the substrate, it would be assigned a score of 2.

Result	**Score**
Splitting cracks top coat, intact base coat, substrate surface not exposed	1
Splitting cracks top coat, crack propagation base coat, substrate surface exposed	2
Splitting cracks base coat, substrate surface exposed	3
Damaged base coat revealing substrate surface, substrate surface exposed	4

Table 1 – Impact scoring

Comparative Example 1

[00111] The metal sheet was coated with the epoxy based intumescent paint. Both components of the epoxy system were mixed according to supplier ratio recommendation using a standard lab mixer and the material applied onto the bare metal surface with a metal spatula. The material was left to dry at least for a week at 25°C before being submitted to impact testing.

Comparative Example 2

[00112] The metal sheet was coated with the intumescent coating A, a polyurethane based intumescent paint. The coating was applied by high pressure hot spray equipment.

[00113] Both components of the system were heated in the equipment to 80°C, pumped to an application spray-gun, in which they are high pressure impingement mixed, before being projected to the metal substrate plates. The material plates are left at least a week at 25°C before being submitted to impact testing.

Example 1

[00114] The metal sheet was coated with an impact protective coating comprising the Huntsman supplied fast curing PU coating. A coating of the two-component epoxy intumescent paint was applied on top.

[00115] Both components of the fast curing PU coating were heated in the equipment to 80°C, pumped to an application spray-gun, in which they are high pressure impingement mixed, before being projected to the metal substrate plates.

[00116] The epoxy coating was applied in the same way as described in Comparative Example 1.

[00117] The material plates were left at least a week at 25°C before being submitted to impact testing.

Example 2

[00118] The metal sheet was coated with an impact protective coating comprising the Huntsman supplied fast curing PU and Huntsman supplied intumescent coating A was applied on top. Both components of the fast curing PU and the Huntsman supplied intumescent coating A were heated in the equipment to 80°C, pumped to an application spray-gun, in which they are impingement mixed, before being projected to the metal substrate plates.

[00119] The material plates are left at least a week at 25°C before being submitted to impact testing.

The results are shown in Table 2 below:

Temp	**Comp. Ex. 1 (Epoxy intumescent)**	**Comp. Ex. 2 (PU intumescent)**	**Ex. 1 (Epoxy intumescent/PU impact)**	**Ex. 2 (PU intumescent/PU impact)**
-35°C	3	4	1	1

Table 2 – Results from impact testing.

[00120] These results demonstrate that the second Polyurethane impact protection layer acts as a shock absorbing layer dissipating the impact energy and assuring that the metal substrate is protected from external exposure in the event of an impact.

[00121] While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the spirit and scope which is determined by the appended claims.

Claims:

1. A multi-coating system comprising: (i) an impact protective coating composition comprising a polyisocyanate component and a polyisocyanate reactive composition comprising one or more polyamines or one or more polyhydric alcohols or a mixture thereof; and (ii) a fire protective coating composition selected from an epoxy adhesive, a polyurethane elastomer, and an intumescent-containing composition comprising (a) an isocyanate component, (b) an isocyanate-reactive hydrogen composition including one or more compounds containing an isocyanate-reactive hydrogen, and (c) an intumescent component.

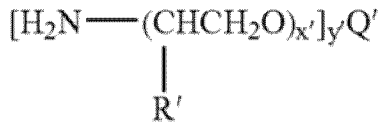
2. The multi-coating system of claim 1, wherein the polyisocyanate component comprises a semi-prepolymer or prepolymer formed from the reaction of a polyisocyanate and a polyhydric alcohol.

3. The multi-coating system of claim 2, wherein the polyhydric alcohol is a polyether polyol.

4. The multi-coating system of claim 2, wherein the polyhydric alcohol is a copolymer of one or more of a polyether polyol, a polyester polyol, a polycarbonate polyol, and a polycaprolactone polyol.

5. The multi-coating system of claim 1, wherein the one or more polyamines comprises a polyoxyalkylene polyamine.

6. The multi-coating system of claim 5, wherein the polyoxyalkylene polyamine is a compound having the formula



where Q' is a polyvalent residue of an isocyanate-reactive hydrogen-containing compound after removal of at least one isocyanate-reactive hydrogen, y' is at least 2, each R' is independently hydrogen, methyl, ethyl or propyl, and x' is from about 1 to about 40.

7. The multi-coating system of any preceding claim, wherein the impact protective coating composition reacts to form an impact protective coating having a glass transition temperature of less than about -30°C, preferably less than about -35°C, more preferably less than about -40°C, preferably less than about -50°C, preferably less than about -60°C

8. The multi-coating system of any preceding claim, wherein the impact protective coating composition further comprises an amine-terminated chain extender.

9. The multi-coating system of any preceding claim, wherein the isocyanate component comprises a prepolymer formed from the reaction of a polyisocyanate and a polyhydric alcohol having a molecular weight from about 400-5000 Da.

10. The multi-coating system of any preceding claim, wherein the one or more compounds containing an isocyanate-reactive hydrogen comprises a polycarbonate polyol, a polycaprolactone polyol, a polytetramethylene ether glycol (PTMEG) or a mixture thereof.

11. The multi-coating system of any preceding claim, wherein the intumescent component comprises at least one or more intumescent ingredients containing phosphorus, nitrogen and boron atoms with a weight ratio of phosphorus to nitrogen in the intumescent component being between 0.5/1 to 1.5/1 and the amount of boron being from about 1% by weight to about 5% by weight, based on the total weight of the fire protective coating composition.

12. The multi-coating system of claim 11, wherein the intumescent component further comprises an acid source selected from ammonium polyphosphate, melamine polyphosphate, magnesium sulphate, boric acid, a phosphorus containing polyol, dihydroxaphosphaphenanthrene oxide and an adduct thereof.

13. The multi-coating system of claim 11 or claim 12, wherein the intumescent component further comprises a gas source.

14. The multi-coating system of any one of claims 11 to 13, wherein the intumescent component further comprises at least one nucleating agent.

15. A process for producing a cured impact resistant intumescent substrate comprising (a) applying a polyisocyanate component and a polyisocyanate reactive composition to at least a portion of a surface of a substrate, (b) allowing the polyisocyanate component and the polyisocyanate reactive composition to cure by allowing a reaction between the polyisocyanate component and the polyisocyanate reactive composition to proceed to form an impact protective coating on the surface

of the substrate; (c) applying an isocyanate component, an isocyanate-reactive hydrogen composition and an intumescent component to at least a portion of a surface of the impact protective layer; and (d) allowing the isocyanate component, the isocyanate-reactive hydrogen composition and the intumescent component to cure by allowing a reaction between the isocyanate component, the isocyanate-reactive hydrogen composition and the intumescent component to proceed to form a fire protective coating on the impact protective coating.

16. A method of coating an external surface of a composite vessel for protection against damage from impact and during a fire situation comprising applying an impact protective coating composition on top of the external surface of the composite vessel and allowing it to from an impact protective coating and applying a fire protective coating composition on top of the impact protective coating and allowing it to form a fire protective coating on top of the impact protective coating wherein: (i) the impact protective coating composition comprises a polyisocyanate component and a polyisocyanate reactive composition; and (ii) the fire protective coating composition is selected from an epoxy adhesive, a polyurethane elastomer, and an intumescent-containing composition comprising: (a) an isocyanate component, (b) an isocyanate-reactive hydrogen composition including one or more compounds containing an isocyanate-reactive hydrogen, and (c) an intumescent component.

17. The method of claim 16, wherein the intumescent component comprises at least one or more intumescent ingredients containing phosphorus, nitrogen and boron atoms with a weight ratio of phosphorus to nitrogen in the intumescent component being between 0.5/1 to 1.5/1 and the amount of boron being from about 1% by weight to about 5% by weight, based on the total weight of the fire protective coating composition.

18. A coated composite vessel made by the process of claim 15, or the method of claim 16 or claim 17.

19. A composite vessel comprising a surface, wherein at least a portion of the surface is coated with an impact protective coating and at least a portion of the impact protective coating is coated with a fire protective coating.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/068010

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G18/48 C08G18/50 C09D5/18 C09D175/08
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)

C08G C09G 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 2017/327700 A1 (JEROMENOK JEKATERINA [DE] ET AL) 16 November 2017 (2017-11-16) paragraphs [0013], [0105] - [0112], [0038]; claims 1-3; compounds D, 2	1-19
X	US 2016/222226 A1 (PRIEMEN STEFAN [BE] ET AL) 4 August 2016 (2016-08-04) paragraphs [0138], [0068], [0126] - [0130]; claims 1-16	1-19
A	CN 101 326 249 A (GUPTA LAXMI C [US]) 17 December 2008 (2008-12-17) claims 1-20	1-19

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

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 August 2024	16/09/2024

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	Buestrich, Ralf

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/068010

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